

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08F 210/02, 8/44, 8/12</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 96/23009</b> <b>(43) International Publication Date:</b> 1 August 1996 (01.08.96)
<b>(21) International Application Number:</b> PCT/US96/01130 <b>(22) International Filing Date:</b> 29 January 1996 (29.01.96)  <b>(30) Priority Data:</b> 08/379,411 27 January 1995 (27.01.95) US  <b>(71) Applicant:</b> CHEVRON CHEMICAL COMPANY [US/US]; P.O. Box 5047, San Ramon, CA 94583-0947 (US).  <b>(72) Inventors:</b> WANG, James, H.; 1325 E. Overland Road, Appleton, WI 54915 (US). ROSENDALE, David; 205 Len Drive, Mauriceville, TX 77632 (US). KURKOV, Victor, P.; 66 Dunfries Terrace, San Rafael, CA 94901 (US). THEARD, Leslie, P.; 10050 Westpark, No. 1003, Houston, TX 77042 (US). CHING, Ta, Yen; 10 Santa Yorma Court, Novato, CA 94945 (US). COMPTON, Lewis, R.; 2705 East Tanager Trails, Orange, TX 77632 (US). PALMGREN, Tor, Henrik, Gustav; 2509 International Avenue, Orange, TX 77632 (US). EICHELBERGER, Mitchell, P.; 42 Meadowridge Place, The Woodlands, TX 77381 (US).  <b>(74) Agents:</b> MICHEL, Marianne, H. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).		<b>(81) Designated States:</b> FI, JP, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> LOW-HAZE IONOMERS OF COPOLYMERS OF ALPHA-OLEFINS, CARBOXYLIC ACID ESTERS, AND OPTIONAL COMONOMERS, AND PROCESSES FOR MAKING AND ACIDIFYING THESE IONOMERS  <b>(57) Abstract</b>  Ionomer compositions which have improved optical properties are disclosed. These compositions comprise ionomers which can be represented as the polymerization product of alpha-olefins having from two to eight carbon atoms, esters of alpha, beta-ethylenically-unsaturated carboxylic acids, metal salts of acrylic and methacrylic acid, and optional alpha, beta-ethylenically-unsaturated comonomers which impart some desired polymer property or properties, such as acidity and/or solvent resistivity. Also disclosed are methods of making these ionomer compositions in a reactive extruder and treating the compositions with acid to impart acidity to the compositions or to only the surface of the compositions.		

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

1     **LOW-HAZE IONOMERS OF COPOLYMERS OF ALPHA-OLEFINS, CARBOXYLIC**  
2     **ACID ESTERS, AND OPTIONAL COMONOMERS, AND PROCESSES FOR**  
3     **MAKING AND ACIDIFYING THESE IONOMERS**

4     This application is a continuation-in-part application of  
5     U.S. Ser. No. 08/330,290, filed Oct. 27, 1994, which is a  
6     continuation-in-part application of U.S. Ser. No.  
7     08/144,173, filed Oct. 27, 1993.

8                     **BACKGROUND**

9     This invention provides new polymeric ionomer compositions  
10    which have low haze. Low haze makes the compositions  
11    especially suited for use in clear packaging films, in  
12    addition to the other applications in which ionomers are  
13    utilized. This invention also provides a method for making  
14    these new polymeric compositions and for modifying the  
15    acidity of the compositions.

16    The compositions comprise ionomers which can be represented  
17    as the polymerization product of alpha-olefins having from  
18    two to eight carbon atoms, esters of alpha, beta-  
19    ethylenically-unsaturated carboxylic acids, metal salts of  
20    acrylic and methacrylic acid, and optional alpha, beta-  
21    ethylenically-unsaturated comonomers which impart some  
22    desired polymer property or properties, such as acidity  
23    and/or solvent resistivity. These ionomer compositions can  
24    easily be formed into films.

25    Ionomers which can be formed into films and methods of  
26    making ionomers are known in the art. Although these  
27    previously-known ionomers have similar chemical constituents  
28    to the ionomer compositions of this invention, the known  
29    ionomers have significantly different properties from the  
30    compositions of this invention. In addition, the known

1 processes for making ionomers are also quite different from  
2 the method of making compositions of the present invention.

3 Japanese patent number Sho 49-31556 to Iwami et al., dated  
4 Aug. 22, 1974, discloses a process for making ionomers which  
5 comprises saponifying copolymers of ethylene and alpha,  
6 beta-ethylenically-unsaturated carboxylate esters with a  
7 basic metal compound in aliphatic alcohol or in an organic  
8 solvent containing an aliphatic alcohol. The copolymer is  
9 homogeneously or heterogeneously dispersed in the alcohol  
10 solution. The saponified product can be further acidified  
11 to provide a composition having acid groups. Although the  
12 ionomers which have acid functionality are said to have low  
13 haze, no haze values are provided for ionomers which have no  
14 acid functionality.

15 Japanese patent number Sho 53-134591 to Harada et al., dated  
16 Nov. 24, 1978, discloses a film made by the process of Sho  
17 49-31556 which is said to be useful for stretch-wrap  
18 applications. Their ionomer comprises a copolymer having  
19 90-98 mole percent ethylene, 9.7 to 2.0 mole percent of an  
20 alkyl ester of an unsaturated carboxylic acid, 0 to 2.5 mole  
21 percent of unsaturated carboxylic acid, and 0.3 to 2.5 mole  
22 percent of a metal salt of an unsaturated carboxylic acid.  
23 It is stated that their film has very good mechanical,  
24 thermal, and optical properties, but the film is limited to  
25 having less than 9.7 mole percent ester to prevent blocking  
26 occurs between film layers. In addition, the copolymer is  
27 limited to a maximum of 2.5 mole percent metal salt of an  
28 unsaturated carboxylic acid above which the viscosity of the  
29 copolymer is too high to allow processing of the copolymer.  
30 All copolymers in the films of the examples contain an  
31 unsaturated carboxylic acid component, which, the patent  
32 states, is used to adjust the modulus of elasticity and  
33 transparency of the film.

1 U.S. patent number 5,218,057, issued to V. Kurkov and  
2 L. Theard on June 8, 1993 and which is incorporated by  
3 reference in its entirety, teaches a process for saponifying  
4 an ethylene alkyl acrylate copolymer which comprises adding  
5 an aqueous solution of an inorganic alkali metal base to a  
6 molten ethylene-alkyl acrylate copolymer and mixing the  
7 alkali metal base and copolymer at a temperature sufficient  
8 for saponification to take place and at which the ethylene-  
9 alkyl acrylate copolymer remains in a molten or fluid state.  
10 Copolymers made by this process have lower tensile strength,  
11 lower gloss, and much higher haze than the copolymers of the  
12 present invention.

13 U.S. patent number 4,638,034 to McClain, dated Jan. 20, 1987  
14 and which is incorporated by reference in its entirety,  
15 claims a process for preparing an ethylene-acrylic acid  
16 copolymer salt which comprises saponifying an ethylene-alkyl  
17 acrylate copolymer in the molten state, in the absence of  
18 solvent or water other than by-product alkanol, with alkali  
19 metal hydroxide or alkaline earth metal hydroxide under non-  
20 static mixing conditions so as to thereby form alkanol and  
21 an alkali metal or alkaline earth metal salt of ethylene-  
22 acrylic acid copolymer, and separately recovering the  
23 alkanol and the salt.

24 U.S. patent number 3,970,626 to Hurst et al., dated July 20,  
25 1976, discloses a copolymer of ethylene, alkyl acrylate or  
26 methacrylate, and an alkali metal salt of acrylic or  
27 methacrylic acid. Although this patent is mainly concerned  
28 with forming copolymers which form stable aqueous emulsions,  
29 the patent states that the copolymer can be extruded into  
30 films of good flexibility. Copolymers in the examples are  
31 formed using a batch autoclave. It is stated that about a  
32 one-fold excess of sodium hydroxide over what is  
33 theoretically required is used to convert the ester groups.

1 U.S. patent number 4,042,766 to Tatsukami et al., dated Aug.  
2 16, 1977 and which is incorporated by reference in its  
3 entirety, provides a method for preparing ionically cross-  
4 linked copolymers comprising melt-blending a copolymer  
5 comprising 1) ethylene and 2) at least one alkyl acrylate or  
6 methacrylate where the alkyl is selected from the group  
7 consisting of isopropyl or tert-butyl, with 3) at least one  
8 metal compound selected from the group consisting of  
9 acetates, formates, and oxides of zinc, magnesium, calcium,  
10 and sodium, and maintaining the molten blend at a  
11 temperature of about 200 to 320°C. The patent states that  
12 high mixing efficiency is desirable in the reaction  
13 equipment to assure uniform dispersion of the metal compound  
14 into the ester copolymer and to assure quick evaporation of  
15 the low molecular-weight byproducts, such as by melt-  
16 blending the components. Per the patent, adequate mixing  
17 was provided by a 20 mm-diameter single-screw extruder  
18 having a retention time of about one minute, as illustrated  
19 in Example 1 of that patent.

20 U.S. patent number 3,789,035 to Iwami et al., dated Jan. 29,  
21 1974 and which is incorporated by reference in its entirety,  
22 discusses three methods for acidifying an ionomer of a  
23 copolymer of ethylene and an ester of an alpha, beta-  
24 ethylenically-unsaturated carboxylic acid. The ionomer is  
25 made by saponifying a copolymer of ethylene and an ester of  
26 an alpha, beta-ethylenically-unsaturated carboxylic acid  
27 with a basic metal compound in a solvent containing an  
28 alcohol. The patent states that the alcohol is used to  
29 promote the reaction of the basic metal compound with the  
30 copolymer. The ionomer is then acidified by either 1)  
31 adding acid and replacing some of the basic metal with  
32 hydrogen; 2) melt-blending a polymer having acid groups with  
33 an ionomer; or 3) exchanging a non-alkali metal ion with the

1 alkali metal ion on the ionomer which has been dispersed in  
2 a solvent.

3 U.S. patent number 3,264,272 to Rees, dated Aug. 2, 1966,  
4 claims a composition comprising a random copolymer of an  
5 alpha-olefin having from two to ten carbon atoms, an alpha,  
6 beta-ethylenically-unsaturated carboxylic acid having from  
7 three to eight carbon atoms in which 10 to 90 percent of the  
8 acid is neutralized with metal ions, and an optional third  
9 mono-ethylenically unsaturated comonomer such as methyl  
10 methacrylate or ethyl acrylate. This copolymer is acidic  
11 due to the carboxylic acid groups present in the copolymer.  
12 U.S. patent number 3,404,134 discloses the process for  
13 making these compositions, which comprises reacting an  
14 ethylene acrylic acid copolymer with a metal compound at a  
15 pressure between 100 and 10,000 psi and a temperature above  
16 the melt-point of the copolymer.

17 U.S. patent number 5,189,113 to Muehlenbernd et al., dated  
18 Feb. 23, 1993, discloses a process for making ionically  
19 cross-linked copolymers of ethylene and alpha, beta-  
20 ethylenically-unsaturated carboxylic acids or alpha, beta-  
21 ethylenically-unsaturated comonomers donating carboxyl  
22 groups, such as anhydrides. This process requires reacting  
23 the copolymer with a solid metal compound in a mixing zone  
24 of a twin-screw extruder and subsequently pumping in water.  
25 The advantages for this process are said to be that no  
26 discoloration of the ionomer occurs because no corrosion of  
27 the twin-screw extruder occurs, and no specks of unreacted  
28 solid metal compound are found in the ionomer film.

29 U.S. patent number 5,003,001 to Hasenbein et al., dated Mar.  
30 26, 1991, claims a process for making ionically cross-linked  
31 copolymers of ethylene and alpha, beta-ethylenically-  
32 unsaturated carboxylic acids or alpha, beta-ethylenically-

1 unsaturated comonomers donating carboxyl groups, such as  
2 anhydrides. This process reacts the copolymer with an  
3 aqueous metal salt solution in a first reaction zone at a  
4 temperature from 140 to 180°C to form ionomer and completely  
5 devolatilizes the ionomer in a second, three-stage  
6 devolatilization zone at a temperature from 200 to 270°C.  
7 This process is said to provide odor-free ionomer film which  
8 is free of specks.

9 Although there has been much research in the area of  
10 ionomers, what has been lacking in the prior art is  
11 optically clear ionomers comprising copolymers of alpha  
12 olefins having two to eight carbon atoms, esters of alpha,  
13 beta-ethylenically-unsaturated carboxylic acids, and metal  
14 salts of alpha, beta-ethylenically-unsaturated carboxylic  
15 acids as well as methods of making those ionomers. This  
16 invention provides such compositions and methods.

#### 17 SUMMARY OF THE INVENTION

18 In one embodiment, the invention comprises a copolymer of  
19 alpha-olefins having from two to eight carbon atoms, esters  
20 of alpha, beta-ethylenically-unsaturated carboxylic acids  
21 having from four to twenty-two carbon atoms, and metal salts  
22 of acrylic or methacrylic acid, wherein this copolymer has a  
23 haze of no more than ten percent as measured by ASTM method  
24 D 1003.

25 In one preferred embodiment, the invention comprises a  
26 copolymer of ethylene, methyl acrylate, and sodium salt of  
27 acrylic acid, wherein the haze of the copolymer is no more  
28 than five percent.

29 In another embodiment, the invention comprises a method of  
30 making an ionomer composition. This method comprises  
31 contacting a Group IA metal-containing solution with a

1 molten or fluid copolymer comprising alpha-olefins having  
2 from two to eight carbon atoms and esters of alpha, beta-  
3 ethylenically-unsaturated carboxylic acids having from four  
4 to twenty two carbon atoms and having a melt index between  
5 about 100 and about 2000 g/10 min., as measured by ASTM  
6 method D 1239 at 190°C using a 2.16 kg weight; and  
7 intensively mixing the copolymer and Group IA metal-  
8 containing solution at a temperature and to an extent which  
9 provides an ionomer composition having no more than ten  
10 percent haze.

11 In another embodiment, the invention comprises a method of  
12 reducing the water solubility of an ionomer composition  
13 formed into a shape such as strands, pellets, or film, which  
14 method comprises contacting a surface of the shape with an  
15 acid.

16 Among other factors, the present invention is based on our  
17 finding that films of the composition as described herein  
18 have very low haze, particularly when the films are made  
19 after saponifying a copolymer as described above under  
20 conditions which include intensive mixing, a greater extent  
21 of saponification, and higher reaction temperatures. Film  
22 haze is no more than ten percent, and many films have a haze  
23 of no more than five or even two percent. Furthermore, in a  
24 preferred embodiment, the composition has improved  
25 properties such as improved tensile strength, hot tack  
26 strength, and/or heat seal strength over ionomers of similar  
27 composition.

28 In addition to the properties discussed above, many of the  
29 compositions of this invention have no acidity, regardless  
30 of the extent of saponification. These advantages and  
31 others are further described below.

### DESCRIPTION OF THE FIGURES

Figure 1 is a scanning electron micrograph of a freeze-fractured cross-section of 3-mil thick film made from an ionomer composition of this invention, taken at a magnification factor of 8,000.

Figure 2 is a scanning electron micrograph of a freeze-fractured cross-section of 3-mil thick film of ionomer of Comparative Example G. Figure 2 illustrates that spherical and oblong ionic clusters or regions are present in the ionomer. This micrograph was also produced at a magnification factor of 8,000.

A JEOL JSM-820 scanning electron microscope was used to generate the micrographs. The micrographs of Figures 1 and 2 show the fracture surface of films which were made by the blown film process of the examples.

Figure 3 shows the hot-tack of ionomer of this invention from Example 20 as a function of temperature. The ordinate is temperature in °C, and the abscissa is hot-tack, measured in Newtons/inch. Line 1 is 35% hydrolyzed ionomer, line 2 is 42% hydrolyzed ionomer, and line 3 is 50% hydrolyzed ionomer.

Figure 4 shows the heat seal strength of the ionomer/polyethylene film of Example 22 as a function of temperature. The ordinate is temperature in °F and the abscissa is the heat seal strength in lb/inch.

### DETAILED DESCRIPTION OF THE INVENTION

#### A. Compositions

Compositions of this invention can be represented as the copolymerization product which contains the following comonomers:

- 1 (a) alpha-olefins having from 2 to 8 carbon atoms,
- 2 (b) esters of alpha,beta-ethylenically-unsaturated
- 3 carboxylic acids,
- 4 (c) metal salts of acrylic or methacrylic acid, and
- 5 (d) optionally, other alpha, beta-ethylenically-unsaturated
- 6 comonomers which impart desirable polymer properties.

7 These compositions have no more than ten percent haze,  
8 preferably no more than seven percent haze, and more  
9 preferably, no more than five percent haze. The most  
10 preferred compositions have no more than two percent haze.  
11 Additionally, these compositions have very good hot tack  
12 strength, heat seal strength, and mechanical properties such  
13 as tensile strength. Acid functionality can also be  
14 introduced into these ionomers.

15 Examples of compositions of this invention include ethylene-  
16 methyl acrylate-sodium acrylate ionomer, ethylene-methyl  
17 methacrylate-sodium methacrylate ionomer, ethylene-ethyl  
18 acrylate-sodium acrylate ionomer, ethylene-propylene-methyl  
19 acrylate-sodium acrylate ionomer, ethylene-propylene-methyl  
20 methacrylate-sodium methacrylate ionomer, ethylene-methyl  
21 acrylate-lithium acrylate ionomer, ethylene-methyl acrylate-  
22 potassium acrylate ionomer, ethylene-methyl acrylate-  
23 cobalt(II) or (III) acrylate ionomer, ethylene-methyl  
24 acrylate-zinc acrylate ionomer, ethylene-methyl acrylate-  
25 titanium(II), (III), or (IV) acrylate ionomer, ethylene-  
26 methyl acrylate-magnesium acrylate ionomer, ethylene-methyl  
27 acrylate-iron(II) or (III) acrylate ionomer, ethylene-methyl  
28 acrylate-nickel(II) or (III) acrylate ionomer, ethylene-  
29 methyl acrylate-copper(I) or (II) acrylate ionomer,  
30 ethylene-methyl acrylate-acrylic acid-sodium acrylate

1 ionomer, ethylene-methyl methacrylate-methacrylic acid-  
2 sodium methacrylate ionomer, ethylene-methyl acrylate-sodium  
3 acrylate ionomer grafted with maleic anhydride, ethylene-  
4 methyl acrylate-maleic anhydride-sodium acrylate ionomer,  
5 and acrylic acid-grafted-(ethylene-methyl acrylate-sodium  
6 acrylate) ionomer.

7 Monomer (a) comprises alpha-olefins having from 2 to 8  
8 carbon atoms. Preferably, monomer (a) comprises alpha-  
9 olefins having from 2 to 3 carbon atoms, and more  
10 preferably, monomer (a) consists essentially of ethylene.

11 Monomer (b) comprises esters of alpha, beta-ethylenically-  
12 unsaturated carboxylic acids having from 4 to 22 carbon  
13 atoms. Preferably, monomer (b) has from 4 to 13 carbon  
14 atoms, and more preferably has from 4 to 8 carbon atoms.  
15 Examples of monomer (b) include methyl acrylate, methyl  
16 methacrylate, ethyl acrylate, ethyl methacrylate, butyl  
17 acrylate, and butyl methacrylate. Methyl acrylate is the  
18 preferred monomer (b).

19 Monomer (c) is a metal salt of acrylic or methacrylic acid.  
20 The metal ion is selected from Group IA, Group IIA, and  
21 transition metal ions. The metal ions may also be aluminum,  
22 gallium, germanium, and tin. Other examples include  
23 lithium, sodium, potassium, rubidium, cesium, calcium,  
24 magnesium, zinc, titanium, iron, cobalt, nickel, and copper.  
25 Preferably, the metal ion is a Group IA or Group IIA metal  
26 ion, and more preferably, the metal ion is a Group IA metal  
27 ion. Most preferred is sodium. Monomer (c) is about 25 to  
28 99 mole percent of the total amount of (b) and (c) present  
29 in a composition. Preferably, monomer (c) is about 35 to  
30 80, and more preferably, is about 40 to 60, mole percent of  
31 the total amount of (b) and (c) present in a composition.

1 Typically, a composition of this invention contains from  
2 about 1 to 20 mole percent of monomers (b) and (c) in total.  
3 Preferably, a composition contains about 3.5 to 12.5 mole  
4 percent, and more preferably, about 5.5 to 10 mole percent  
5 of monomers (b) and (c). Most preferred is a composition  
6 containing about 7.5 to 10 mole percent of monomers (b) and  
7 (c).

8 Monomer (d) is an alpha, beta-ethylenically-unsaturated  
9 comonomer which imparts certain desired polymer properties.  
10 The amount and type of monomer (d) are determined by the  
11 particular properties that are desired in the final  
12 composition. For example, monomer (d) may be acrylic or  
13 methacrylic acid which is present in an amount that provides  
14 the desired acid functionality to the composition. Other  
15 examples of monomer (d) include maleic anhydride and maleic  
16 acids to impart acidity, acrylonitrile to impart solvent  
17 resistance, and styrene to increase the rigidity of the  
18 composition. Typically, the compositions contain 0 to 10  
19 mole percent of monomer (d). Preferred compositions contain  
20 0 to 5 mole percent of monomer (d).

21 Monomer (d) can also be added by grafting a group such as  
22 acrylic acid or maleic anhydride to a composition of the  
23 present invention or to one of the composition's precursors.  
24 As a result, compositions can comprise grafted (ethylene,  
25 (meth)acrylate, metal salt of (meth)acrylic acid)  
26 copolymers. Maleic anhydride-grafted (ethylene, methyl  
27 acrylate, sodium acrylate) copolymer is one such  
28 composition.

29 The ionomer compositions of this invention have a number of  
30 surprising features which distinguish them from other  
31 ionomers having similar chemical constituents. The ionomers  
32 of this invention are quite clear. Haze is typically no

1 more than 5 percent. Also, in one preferred embodiment, the  
2 60° gloss is typically at least 100, and in many instances,  
3 is at least 120. In another preferred embodiment, tensile  
4 strength of the composition is improved over ionomers of  
5 similar composition by 100-300 percent. Hot-tack strength  
6 and heat seal strength can also be improved over ionomers of  
7 similar composition. Combinations of these improved  
8 features are present in some preferred compositions of this  
9 invention.

10 For example, the haze, gloss, and tensile strength of  
11 ionomer of this invention are substantially different from  
12 the haze, gloss, and tensile strength of ionomer made by the  
13 process of U.S. Pat. № 5,218,057. Ethylene-methyl acrylate  
14 copolymer having about 20 weight percent (about 7.5 mole  
15 percent) methyl acrylate and having about 65% of the methyl  
16 acrylate saponified with aqueous sodium hydroxide according  
17 to the process of U.S. Pat. № 5,218,057 had a haze of 15%  
18 and 60° gloss of 66. Tensile strength of an ethylene-methyl  
19 acrylate copolymer having 20 weight percent methyl acrylate  
20 which had about 60% of the methyl acrylate groups saponified  
21 with aqueous sodium hydroxide according to the process of  
22 U.S. Pat. № 5,218,057 was 1582 psi in the machine direction.  
23 A composition of the present invention made by saponifying  
24 an ethylene-methyl acrylate copolymer having about 20 weight  
25 percent methyl acrylate with aqueous sodium hydroxide to  
26 convert about 65% of the methyl acrylate groups had a haze  
27 of 2%, gloss of 133, and tensile strength in the machine  
28 direction of 4010 psi.

29 The ionomers of this invention also can be formed into very  
30 thin film. When blowing film, the blow-up ratio can be as  
31 high as 2:1 to about 2.5:1. Typically, a film of ionomer of  
32 this invention can have a thickness of less than about 1  
33 mil. Film having a thickness of about 0.5 mil has been

1 made, and film having a thickness of about 0.2 - 0.3 mil can  
2 be made on conventional processing equipment.

3 The morphology of prior art ionomers can also differ  
4 substantially from the morphology of ionomers of this  
5 invention. Prior-art ionomers can contain highly localized  
6 and large clusters of ionic material dispersed throughout  
7 the ionomer. Scanning-electron micrographs have shown that  
8 these clusters can range in size from about 0.05 micron to  
9 greater than 1 micron in size.

10 Figure 2 is a scanning-electron micrograph for the ionomer  
11 of Comparative Example G. This ionomer consists essentially  
12 of ethylene, 5.7 mole percent methyl acrylate, and 1.8 mole  
13 percent of the sodium salt of acrylic acid. The spherical  
14 or oblong ionic clusters evident in this micrograph range in  
15 size from about 0.1 micron to about 0.5 micron. The  
16 clusters were determined to be ionic by energy-dispersive  
17 X-ray spectroscopy, which showed a higher sodium content  
18 within the clusters when compared to the surrounding  
19 continuous phase.

20 Figure 1 is a scanning-electron micrograph for ionomer  
21 composition of this invention, which consists essentially of  
22 ethylene, 3.7 mole percent methyl acrylate, and 3.7 mole  
23 percent of the sodium salt of acrylic acid. This ionomer  
24 composition is substantially free of ionic clusters of the  
25 size seen in Figure 2, since essentially no ionic clusters  
26 are observed in this micrograph. An ionomer composition  
27 which is substantially free of ionic clusters contains  
28 essentially no ionic clusters about 0.05 micron in size or  
29 larger when a freeze-fractured cross-section of 3-mil thick  
30 blown film which is made by the method of Example 1 is  
31 viewed with a scanning electron microscope at a  
32 magnification factor of 8,000. An ionomer composition which

1 is substantially free of ionic clusters will also have a  
2 haze of no more than ten percent. The ionomer composition  
3 of Figure 1 corresponds to the composition of Example 12,  
4 which had a haze of 3%. The large flecks of debris in  
5 Figure 1 are believed to be foreign matter. The flecks are  
6 not regions having high sodium content.

7 Additives well-known in the art may be included in the  
8 ionomer, such as anti-block and slip additives and anti-  
9 oxidants. Preferably, the composition of this invention  
10 also contains a polymeric acid having a molecular weight of  
11 less than about 10,000, such as ethylene acrylic acid.  
12 Ionomer compositions containing these low molecular weight  
13 acids are disclosed in copending U.S. Ser. No. 08/188,848,  
14 filed Jan. 31, 1994, which is incorporated by reference in  
15 its entirety herein.

16 B. Method for making the compositions

17 One method for making compositions of this invention  
18 comprises saponifying a copolymer having ester groups with a  
19 Group IA metal-containing solution. To obtain the clear  
20 ionomer compositions of this invention, it is important to  
21 provide intensive mixing of the copolymer and the Group IA  
22 metal-containing solution and to have a temperature and/or  
23 extent of saponification high enough that a substantially  
24 uniform saponification of the copolymer occurs. This method  
25 minimizes the production of localized ionomer regions or  
26 domains, which appear as the spherical and oblong ionic  
27 clusters of Figure 2. This method also permits a greater  
28 extent of saponification of the copolymer without obtaining  
29 a saponified product that has so high of a viscosity that it  
30 cannot be formed into a film on conventional equipment.

31 Intensive mixing of the reaction components results from  
32 selection of reactants with the appropriate physical and

chemical characteristics and selection of the proper processing conditions. Particular processing conditions are discussed below for a reactive extruder. However, the general principles disclosed therein apply to processes which are equivalent to saponifying a copolymer with a Group IA metal-containing solution in a reactive extruder..

(1) Reactants

(a) Copolymer to be saponified

The copolymers which are saponified comprise copolymers of ethylene, esters of alpha, beta-ethylenically-unsaturated carboxylic acids, and optional alpha, beta-ethylenically-unsaturated comonomers which impart desirable polymer properties. Typically, these copolymers contain from about 1 to 20 mole percent of esters of alpha, beta-ethylenically-unsaturated carboxylic acids in total. Preferably, the copolymers contain about 2 to 20 mole percent, more preferably 3.5 to 12.5 mole percent, and even more preferably, about 5.5 to 12.5 mole percent of esters of alpha, beta-ethylenically-unsaturated carboxylic acids in total. Most preferred are those copolymers containing about 6.5 to 10 mole percent of esters of alpha, beta-ethylenically-unsaturated carboxylic acids. The preferred esters are alkyl acrylates. Preferably, the alkyl group contains from one to eight carbon atoms, and more preferably contains from one to four carbon atoms. Methyl is a preferred alkyl group.

Examples of the copolymers which are saponified include ethylene-methyl acrylate copolymer, ethylene-methyl methacrylate copolymer, ethylene-ethyl acrylate copolymer, ethylene-propylene-methyl acrylate copolymer, ethylene-propylene-methyl methacrylate copolymer, ethylene-methyl acrylate-acrylic acid copolymer, ethylene-methyl methacrylate-methacrylic acid copolymer, maleic anhydride-

1 grafted-ethylene-methyl acrylate copolymer, ethylene-methyl  
2 acrylate-maleic anhydride copolymer, acrylic acid-grafted-  
3 ethylene-methyl acrylate copolymer, and ethylene-methyl  
4 acrylate-butyl acrylate copolymer. Preferably, the  
5 copolymers are ethylene-methyl acrylate copolymer, ethylene-  
6 methyl methacrylate copolymer, ethylene-ethyl acrylate  
7 copolymer, maleic anhydride-grafted-ethylene-methyl acrylate  
8 copolymer, and ethylene-methyl acrylate-butyl acrylate  
9 copolymer. Most preferred is ethylene-methyl acrylate  
10 copolymer.

11 The melt index of copolymers to be saponified should be  
12 between about 100 and 2000, preferably between about 200 and  
13 800, and more preferably between about 300 and 600 grams/10  
14 minutes. Copolymers having higher melt-index values are  
15 preferred when it is desired to have a saponified  
16 composition with a higher melt index. One process for  
17 making these copolymers comprises polymerizing ethylene,  
18 alkyl acrylate and/or alkyl methacrylate, and the optional  
19 comonomer in autoclaves using free-radical initiation  
20 catalysts. This process is described in U.S. Patent  
21 # 3,350,372, which is incorporated by reference in its  
22 entirety. The copolymers of the examples were made by this  
23 method, unless specified otherwise. In one preferred  
24 embodiment, the ethylene-alkyl acrylate copolymer is made by  
25 the process described in copending U.S. Ser. No. 07/947,870,  
26 filed Sep. 21, 1992 (published as WO 93/06137), which is  
27 incorporated by reference in its entirety herein. Copolymer  
28 made by this process has a substantially higher melt-point  
29 temperature than the copolymer made by the process of U.S.  
30 Patent No. 3,350,372. The ionomer of this invention has  
31 high melt point temperature and high clarity when made with  
32 this copolymer. Another process for producing copolymers  
33 useful in making the ionomer compositions of this invention  
34 comprises free-radical polymerization of ethylene and alkyl

1 acrylate and/or alkyl methacrylate as described above,  
2 followed by reactive extrusion with a compound such as  
3 acrylic acid or maleic anhydride. Alternatively, grafting  
4 may be performed after saponification. A particularly  
5 preferred copolymer is ethylene-methyl acrylate copolymer  
6 having between about 5.5 and 12.5 mole percent methyl  
7 acrylate and having a melt index of about 400 g/10 min.,  
8 available from Chevron Chemical Company as EMAC® copolymer.

9 (b) Group IA metal-containing solution

10 The Group IA metal-containing solution comprises a Group IA  
11 metal in a solvent, which solvent does not prevent  
12 saponification of an ester by the Group IA metal. The  
13 solvent is preferably one which evaporates readily under  
14 devolatilization conditions typically encountered in  
15 reactive extruders. Solvents can be organic or inorganic,  
16 and common solvents include water, alcohols, and  
17 polyethylene glycols, with water being preferred.

18 The Group IA metal-containing solution has at least one  
19 Group IA metal present. Preferably, the solution comprises  
20 an aqueous solution of a Group IA metal oxide and/or  
21 hydroxide, such as oxides and hydroxides of lithium, sodium,  
22 potassium, rubidium, and/or cesium. Preferably, the  
23 Group IA metal-containing solution comprises aqueous sodium  
24 hydroxide or aqueous potassium hydroxide.

25 It is important that the overall concentration of metals in  
26 the Group IA metal-containing solution is low enough that  
27 the solution is capable of being mixed uniformly and  
28 intensively with melted copolymer in a reaction section of a  
29 reactive extruder. However, it is preferred to have only  
30 that amount of solvent present that is necessary to provide  
31 this capability. Normally, a sufficient quantity of solvent  
32 is present when the Group IA metal-containing solution

1 contains little or no excess solvent beyond that required to  
2 solubilize essentially all of the Group IA metal and other  
3 metals present. Thus, for example, 50% aqueous caustic  
4 solution is preferred over 35% aqueous caustic solution.

5 The Group IA metal-containing solution may optionally  
6 contain other metal oxides, hydroxides, and/or salts which  
7 supply cations for monomer (c). The metal ions can be  
8 alkaline earth or transition-element metals. Specific  
9 examples of these metals include calcium, magnesium, zinc,  
10 titanium, cobalt, nickel, and copper. Typical anions  
11 include hydroxide, halide, acetate, propionate, decanoate,  
12 and stearate ions, with acetate ions being preferred anions.  
13 The hydroxide form is also preferred.

14 Instead of being present in the Group IA metal-containing  
15 solution, metal ions (including Group IA metal ions) may  
16 optionally be incorporated into the ionomer composition of  
17 this invention by other methods. One method is to first  
18 saponify a copolymer by the method of this invention, then  
19 totally or partially replace the ion of this ionomer  
20 composition with other metal ions under ion-exchange  
21 conditions, or to react the ionomer composition with an  
22 aqueous metal hydroxide. For example, an ion-exchange  
23 solution comprising an aqueous solution of zinc oxide or  
24 zinc acetate may be mixed with a sodium ionomer composition  
25 of this invention in a section of a reactive extruder to  
26 replace at least a portion of the sodium ions with zinc  
27 ions.

28 Examples of metal ions which may be exchanged include the  
29 alkaline metals, alkaline earth metals such as magnesium,  
30 transition metals such as titanium, cobalt, copper, and  
31 zinc, and other metal ions such as aluminum, gallium,  
32 germanium, and tin.

1 The anion of a salt used to ion-exchange the ionomer is  
2 preferably one which is easily washed out of the ionomer and  
3 separated from it during filtration. Alternatively, the  
4 anion is preferably one which forms an easily-evolved  
5 compound or one which evolves or whose products of  
6 decomposition evolve at devolatilization conditions in a  
7 reactive extruder. Typical anions include chloride,  
8 acetate, propionate, decanoate, and stearate ions. Acetate  
9 ions are preferred.

## 10 (2) Reactive Extruder

11 A reactive extruder which is useful in producing  
12 compositions of this invention comprises an extruder having  
13 a copolymer feed section, one or more reaction sections, a  
14 subsequent devolatilization section, and an extrusion  
15 section. Typically, these sections are separately jacketed  
16 to allow for heating or cooling within each section. These  
17 sections can also be vented with one or more vent ports per  
18 section to allow the escape of volatile components, such as  
19 the solvent for the Group IA metal solution and byproducts  
20 of the saponification reaction, such as alcohols.  
21 Generally, the reactive extruder will also have optional  
22 means for introducing reactants into any reaction sections  
23 as well as means for mixing components in the reaction  
24 section(s) and means for conveying the components through  
25 the extruder. Typically, the means for mixing and conveying  
26 components to be reacted are screws.

27 Reactive extruders can have a single screw or multiple  
28 screws. Each screw typically has a central shaft with a  
29 key-way or spline upon which mixing elements are secured.  
30 The reactive extruder may have either co-rotating or  
31 counter-rotating screws.

1 Typically, copolymer to be reacted is fed to the screw  
2 through a loss-in-weight feeder, and the solid copolymer is  
3 melted in a feed section of the reactive extruder. In some  
4 embodiments, all reactants (i.e. copolymer and Group IA  
5 metal-containing solution) can be fed to the reactive  
6 extruder through a feed section. In a preferred embodiment,  
7 copolymer is introduced into the reactive extruder in a feed  
8 section, and the Group IA metal-containing solution is fed  
9 to one or more reaction sections. A devolatilization  
10 section is a convenient means for removing any solvent and  
11 byproducts of the saponification reaction from the  
12 saponified composition. Equivalent or additional means for  
13 removing volatile components can be used, however, such as  
14 drying the ionomer composition under reduced pressure in a  
15 falling-film evaporator.

16 One reactive extruder which was particularly effective in  
17 producing compositions of this invention is a Werner-  
18 Pfleiderer co-rotating and intermeshing twin-screw extruder.  
19 The reactive extruder had a feed section, a reaction  
20 section, a devolatilization section, and a pressurization or  
21 pumping section which pushed the product through an  
22 extrusion die. The devolatilization section had a first  
23 portion which was vented to a condenser maintained at  
24 atmospheric pressure, and a second portion of the  
25 devolatilization section was vented with sufficient vacuum  
26 and capacity to remove essentially all of the volatile  
27 components from compositions prior to conveying and  
28 extruding them.

29 Typically, copolymer pellets are introduced into a feed  
30 section of a reactive extruder, where the pellets are heated  
31 and worked by the screw to form molten or fluid copolymer.  
32 The screw elements also convey the molten copolymer from  
33 this feed section to a first reaction section, where the

1 molten copolymer and Group IA metal-containing solution are  
2 mixed intensively.

3 Intensive mixing can be supplied by incorporating one or  
4 more reverse-flow elements along with neutral or reverse-  
5 flow kneading blocks on the screw in a reaction zone. The  
6 copolymer to be saponified and the Group IA metal-containing  
7 solution should be mixed as uniformly and as quickly as  
8 possible to provide a fairly uniform reaction of metal-  
9 containing solution with the molten copolymer. Mixing  
10 should be of sufficient intensity that saponification of  
11 only localized areas is prevented.

12 This intensive mixing is of greater intensity than that  
13 required in the prior-art processes of U.S. Pat. # 4,638,034  
14 and U.S. Pat. # 4,042,766. For example, a Werner-Pfleiderer  
15 Model ZSK-40 twin-screw reactive extruder had the  
16 configuration of screw elements detailed in Table 1 column  
17 A. This screw design provided intensive mixing of the  
18 Group IA metal-containing solution with copolymer in the  
19 reaction section through a combination of left-handed  
20 elements and neutral kneading blocks. It is believed that  
21 the left-handed elements in the reaction section provide  
22 momentary retardation of polymer flow in addition to a shear  
23 zone due to impeded and/or reversed flow of the reaction  
24 mass, while the neutral kneading blocks imparted intensive  
25 mixing and promoted additional shear. Most of the  
26 compositions of this invention were produced at a screw  
27 speed of about 400 to 550 rpm. High screw speeds help to  
28 assure intensive mixing.

TABLE 1

ELEMENT NUMBER	COLUMN A	COLUMN B	COLUMN C
1	40/20 <sup>1</sup>	PKR/10 <sup>2</sup>	PKR/10
2	60/60	20/10	20/10

	ELEMENT NUMBER	COLUMN A	COLUMN B	COLUMN C
1	3	60/60	42/42	42/42
2	4	40/40	42/42	42/42
3	5	40/40	42/42	28/28
4	6	40/40	28/28	28/28
5	7	40/20	28/28	28/28
6	8	40/40	20/20	20/20
7	9	25/25	20/20	20/20
8	10	KB45/5/40 <sup>3</sup>	20/20	20/20
9	11	KB45/5/40	KB45/5/28	20/10
10	12	25/25	KB45/5/28	KB45/5/28
11	13	25/25	20/20	KB45/5/28
12	14	25/25	20/20	20/20
13	15	40/20 LH <sup>4</sup>	KB90/5/28	20/20
14	16	25/25	20/10 LH	20/10 LH
15	17	KB90/5/40	20/20	20/10 LH
16	18	25/25	20/20	20/10 LH
17	19	KB90/5/40	KB45/5/28	20/20
18	20	25/25	20/10	20/20
19	21	40/20 LH	20/20	KB45/5/28
20	22	25/25	20/20	20/10
21	23	KB90/5/40	KB90/5/28	20/20
22	24	25/25	20/20	20/20
23	25	KB90/5/40	KB45/5/14 LH	KB90/5/28
24	26	25/25	KB45/5/14 LH	20/20
25	27	40/20 LH	20/20	KB45/5/14 LH
26	28	KB45/5/20 LH	20/20	KB45/5/14 LH
27	29	25/25	KB90/5/28	20/20
28	30	25/25	20/20	20/20
29	31	25/25	20/20	KB90/5/28
30	32	25/25	20/20	20/20
31	33	25/25	20/20	20/20
32	34	40/40	20/20	20/20
33	35	40/40	KB90/5/28	20/20
34	36	40/40	20/20	KB90/5/28
35	37	KB45/5/20 LH	20/20	20/20
36	38	40/40	20/20	20/20
37	39	40/40	20/20	20/20
38	40	40/40	20/20	20/20
39	41	40/40	20/20	KB90/5/28
40	42	25/25	20/20	20/20
41	43	25/25	20/20	20/20
42	44	25/25	KB90/5/28	20/10
43	45	25/25	20/20	20/20
44	46	25/25	20/20	20/20
45	47	25/25	20/10 LH	20/20
46	48	25/25	20/10 LH	20/20
47	49	25/25	20/20	20/20
48	50	25/25	20/20	20/20
49	51	25/25	20/20	20/20
50	52	25/25	20/20	20/20

	ELEMENT NUMBER	COLUMN A	COLUMN B	COLUMN C
1	53	25/25	42/42	20/20
2	54	25/25	42/42	20/20
3	55	25/25	42/42	42/42
4	56		20/20	42/42
5	57		20/20	42/42
6	58		20/20	28/28
7	59		20/20	20/20
8	60		20/20	20/20
9	61			20/20

## NOTES:

1. All elements were right-handed elements unless designated otherwise. The first number is the pitch, given in distance (mm) traveled in one revolution. The second number is the length of the element (mm).
2. The PKR element is a wedge-shaped adapter which provides a taper from the 1/2 inch shaft to the first element of the screw.
3. KB indicates a kneading block. The first number is the angle formed by the paddles on the kneading block when compared to the line through the screw shaft, in degrees. The second number is how many paddles are on one element. The third number is the length of the element (mm).
4. "LH" indicates a left-handed element.

(3) Reaction conditions

Reaction temperature, feed-rate of reactants, and extent of saponification are also important processing parameters when making compositions of this invention.

(a) Reaction temperature

Compositions of this invention are typically produced where the barrel temperature in the reaction section(s) of the extruder is between about 200 and 350°C, although some clear ionomers were prepared at a temperature between about 150 and 200°C. Any reaction temperatures discussed herein refer

1 to the barrel temperatures of the extruder. The actual  
2 temperature of the melted polymer is believed to be lower  
3 than the measured barrel temperature because of heat-  
4 transfer limitations.

5 Preferably, the reaction temperature is between 225 and  
6 350°C, and, more preferably, the temperature is between  
7 about 275 and 350°C. The upper limit of the temperature  
8 range is determined by the temperature at which the  
9 copolymer or composition degrades. The lower limit of the  
10 temperature range is the temperature at which 1) the  
11 copolymer to be reacted is in a molten or fluid state;  
12 2) essentially all of the Group IA metal in the Group IA  
13 metal-containing solution is consumed by the saponification  
14 reaction within the reaction section; and 3) the composition  
15 being extruded remains visually clear. As a general rule,  
16 higher reaction temperatures as specified in the more  
17 preferable range above provide low-haze ionomers more  
18 consistently than lower reaction temperatures.

19 (b) Feed rate of reactants

20 The Group IA metal-containing solution is fed in an amount  
21 that is effective to achieve the desired extent of  
22 saponification of the copolymer being fed to the reactive  
23 extruder. Typically, essentially all of the Group IA metal  
24 in solution reacts with the copolymer. The Group IA metal-  
25 containing solution may be fed to a reaction section batch-  
26 wise or continuously, or it may be fed intermittently so  
27 that the solution is mixed intimately and rapidly with the  
28 molten copolymer. A continuous feed is preferred. The  
29 Group IA metal-containing solution may also be split between  
30 multiple reaction sections and be fed continuously and/or  
31 intermittently to any reaction section.

1 The copolymer to be saponified is fed to the reactive  
2 extruder at a rate high enough that the molten polymer forms  
3 a molten polymer seal between consecutive segments of a  
4 reaction section and between a reaction section and a  
5 devolatilization section. This seal can be formed by having  
6 a reverse-flow screw element at the desired seal location.  
7 The feed-rate should also be low enough that the reaction  
8 mass comprising the copolymer to be saponified and the  
9 Group IA metal-containing solution does not move through the  
10 reaction section so quickly that the reaction mass is not  
11 mixed intensively. The feed-rate should also be low enough  
12 that the extruded polymer is visually clear, corresponding  
13 to no more than ten percent haze.

14 The copolymer to be saponified may be fed to the extruder  
15 batch-wise, intermittently or continuously. A continuous  
16 feed is preferred to provide a commercially-attractive  
17 process which is easily and effectively controlled.

18 Typically, the average residence time for reactants in a  
19 Werner & Pfleiderer ZSK-40 twin-screw extruder which has a  
20 feed section, one reaction section, devolatilization  
21 section, and pumping section is about 30 to about 40 seconds  
22 at a continuous feed-rate of approximately 100 lb./hr. of  
23 polymer to be saponified and at a screw speed of about 500  
24 rpm. The average residence time in the reaction section of  
25 this reactive extruder at these conditions is typically  
26 about 5 to about 15 seconds.

27 When the feed-rate is too high to make a composition of this  
28 invention, the screw torque will decrease, and the ionomer  
29 will turn cloudy. Both of these conditions can be observed  
30 almost immediately upon feeding too much copolymer to the  
31 extruder. Visually, the extruded copolymer turns from clear  
32 to cloudy, and when a strand of the cooled copolymer is

1 pulled in the direction in which it was extruded, the cloudy  
2 copolymer turns whitish and opaque.

3 (c) % saponified

4 The extent of saponification is defined as the percent of  
5 moles of esters of alpha, beta-ethylenically-unsaturated  
6 carboxylic acids converted to metal salts of acrylic and  
7 methacrylic acid. Compositions of this invention have been  
8 produced where the extent of saponification of the ester  
9 groups in the copolymer has been between about 25 and 99%.  
10 Ionomer which has an extent of saponification below about  
11 25% above are typically cloudy and have poorer gloss, melt  
12 strength, and/or tensile strength than compositions of this  
13 invention. A greater extent of saponification generally  
14 produces low-haze ionomers more consistently than a low  
15 extent of saponification, particularly when the reaction  
16 temperature is between about 150 and 225°C.

17 C. Acidification

18 Acidification of a polymer is a useful method for modifying  
19 polymer properties. In one preferred embodiment, ionomers  
20 of this invention have essentially no acidity. These  
21 ionomers can be represented as copolymers comprising  
22 comonomers of alpha-olefins, esters of alpha, beta-  
23 ethylenically-unsaturated carboxylic acids, and metal salts  
24 of alpha, beta-ethylenically-unsaturated carboxylic acids.  
25 The properties of these non-acidic ionomers can be modified  
26 by adding acid groups.

27 Also, some of the ionomers of this invention are highly  
28 water-dispersible. This can be an advantage for  
29 applications where repulpable compositions are desired, such  
30 as repulpable paper coatings and adhesives. However, water  
31 dispersibility is a problem where the ionomer composition is  
32 cooled in a water-bath after saponification, which is a

1 common commercial method of cooling polymers. Much of the  
2 ionomer to be cooled can end up dispersed in the cooling  
3 water, turning the water a milky white color.

4 Other cooling means may be used for handling highly water-  
5 dispersible ionomers, such as hot-face cutting or utilizing  
6 an air-cooled conveyor or a conveyor which has a water-  
7 chilled surface to cool the polymer strands or pellets.  
8 However, these methods are more expensive and less efficient  
9 than passing hot polymer in the form of strands, pellets, or  
10 film through a water bath, and these methods require the  
11 installation of new equipment in many existing commercial  
12 ionomer production facilities. In addition, ionomer may  
13 discolor when using these cooling means, since the ionomer  
14 rapidly oxidizes when it is maintained at elevated  
15 temperatures for the extended periods of time inherent in  
16 these other cooling means.

17 (1) Cooling ionomer in an aqueous acid bath

18 In a preferred embodiment, highly water-dispersible ionomer  
19 of this invention may be cooled in an acid bath to prevent  
20 dispersion of much of the ionomer. Highly water-dispersible  
21 ionomer typically has a high sodium acrylate content which  
22 makes the ionomer water-soluble. It is believed that ion  
23 exchange occurs predominantly on the surface of the polymer  
24 when passing hot ionomer strands through the acid bath,  
25 replacing metal ions on the surface of the polymer with  
26 hydrogen ions from the acid. It is believed that this makes  
27 the surface of the strands or pellets acidic and  
28 substantially reduces their water solubility.

29 Infrared analysis of ionomer pellets which were cooled in an  
30 acid bath detected no acid groups. However, it is believed  
31 that the concentration of acid groups in the overall ionomer

1 pellets was so small that it was undetectable by infrared  
2 analysis of the bulk ionomer.

3 Almost any inorganic or water-soluble organic acid can be  
4 used in the acid bath. A dilute aqueous solution of a non-  
5 oxidizing acid is preferred to reduce processing cost and to  
6 improve the washing efficiency when rinsing any excess acid  
7 off of the polymer. The following list is illustrative of  
8 the types of acids which may be used: sulfuric acid, formic  
9 acid, propionic acid, oxalic acid, and the like. Preferred  
10 acids are hydrochloric acid, phosphoric acid, and acetic  
11 acid.

12 The temperature of the acid solution is preferably that  
13 temperature which produces ionomer which has not discolored  
14 and which provides ionomer at the appropriate temperature  
15 for any subsequent processing steps, such as drying. The  
16 temperature of the acid solution is typically between about  
17 5 to 50°C, and preferably is between about 10 and 30°C.

18 Example 16 illustrates this method for cooling ionomer using  
19 an aqueous acid solution.

20 (2) Acidification of a clear copolymer of  
21 ethylene and esters and metal salts of alpha,  
22 beta-ethylenically-unsaturated carboxylic  
23 acids

24 In one embodiment, compositions of this invention have  
25 carboxylic acid groups, in which case the compositions can  
26 be represented as copolymers comprising comonomers of alpha-  
27 olefins, esters of alpha, beta-ethylenically-unsaturated  
28 carboxylic acids, metal salts of alpha, beta-ethylenically-  
29 unsaturated carboxylic acids, and alpha, beta-ethylenically-  
30 unsaturated carboxylic acids. Acid groups can plasticize  
31 the composition and increase its melt index. This permits

1 tailoring of polymer properties such as polymer flow  
2 viscosity, tear strength, polymer reactivity with food, and  
3 odor or taste for a particular application.

4 Acidification of a composition comprising a copolymer of  
5 alpha-olefins, esters of alpha, beta-ethylenically-  
6 unsaturated carboxylic acids, and metal salts of alpha,  
7 beta-ethylenically-unsaturated carboxylic acids can occur in  
8 a reaction section of a reactive extruder. Preferably,  
9 acidification occurs in a second reaction section when using  
10 reactive extrusion, and preferably after the composition  
11 comprising the reaction product of a copolymer of alpha-  
12 olefins and esters of alpha, beta-ethylenically-unsaturated  
13 carboxylic acids has been saponified with a Group IA metal-  
14 containing solution in a first reaction section.

15 Other equipment may be used in place of a reactive extruder  
16 for acidification of a saponified composition. For example,  
17 a Brabender Plasticorder, a resin kettle, or an autoclave  
18 may be used.

19 A non-oxidizing acid can be used at a temperature and in a  
20 concentration which does not cause significant degradation  
21 of the copolymer or composition. Typically, the amount of  
22 acid required is the amount which provides the desired  
23 weight percent of acid groups per combined weight of acid  
24 and copolymer to be acidified. Examples of these acids  
25 include phosphoric acid, hydrochloric acid, benzoic acid,  
26 lactic acid, and stearic acid. Polymeric non-oxidizing  
27 acids can also be used, such as ethylene-acrylic acid  
28 copolymer, exemplified by Dow Chemical Company's Primacor  
29 Grade 3330. The non-oxidizing acids may have only one or  
30 two monomer units, such as benzoic acid or acetic acid, or  
31 they may comprise polymeric acids having multiple monomer  
32 units and having a molecular weight well in excess of one

1 million, such as Primacor Grade 3330. Phosphoric acid,  
2 lactic acid, and polymer acids are preferred. Typical  
3 temperatures for acidification are between about 190 and  
4 300°C, and preferably are between about 230 and 300°C. The  
5 acid concentration is preferably between 10 and 95%.

6 In certain applications or compositions of this invention,  
7 any byproducts of acidification can remain in the  
8 composition. For other applications or compositions, any  
9 byproducts of acidification and/or any excess acid can be  
10 removed from the ionomer by washing with water or other  
11 solvent and filtering the composition. For example, polymer  
12 acidified using phosphoric acid can be washed with water in  
13 an autoclave. The byproduct salt in the aqueous phase can  
14 subsequently be separated from the polymer by filtration.

15 D. Uses of the compositions

16 Ionomer compositions of this invention can be formed into  
17 single or multi-layer films using conventional equipment.  
18 For example, cast, extruded, or blown film can be made.

19 An ionomer composition of this invention can be coextruded  
20 with or laminated to other polymers such as nylon  
21 (unoriented and oriented), polyester (unoriented and  
22 oriented), polystyrene, polyvinyl acetate,  
23 polyacrylonitrile, polyvinylidene dichloride, and  
24 polyolefins such as polypropylene (unoriented and oriented),  
25 polyethylene (low density, high density, and linear low  
26 density), ethylene-methyl (meth)acrylate copolymers,  
27 ethylene-ethyl (meth)acrylate copolymers, ethylene-  
28 (meth)acrylic acid copolymers, ethylene-vinyl alcohol  
29 copolymers, ethylene vinyl acetate copolymers, and other  
30 polymers and their derivatives capable of being coextruded.  
31 Typical uses for ionomer compositions of this invention  
32 include their use in single-layer or multi-layer films,

1 where they can be used as tie layers or used for imparting  
2 flexibility, toughness, strength, hot tack, and/or heat seal  
3 capabilities. Such uses include stretch films, bundling  
4 (shrink) wrap, food and drug packaging, and skin packaging  
5 for protecting the contents of a package. A layer of  
6 ionomer of this invention can withstand higher temperatures  
7 encountered in some end-uses, such as cook-in bags or  
8 autoclave sterilization. Also, the ionomer of this  
9 invention has high adhesion to other organic materials such  
10 as other polymers or even natural polymers such as the  
11 protein found in meat and cheese.

12 Single-layer ionomer film or multi-layer film in which the  
13 ionomer is on one face of the film can be used as a surface  
14 protection layer for products such as glass, polycarbonate  
15 or poly(methyl methacrylate) products, which can be used in  
16 windshields for vehicles or windows. The ionomer layer  
17 protects products from scratches and/or nicks because of the  
18 ionomer's abrasion resistance. The ionomer's adhesion to  
19 such substrates is excellent, yet it can be peeled readily  
20 from the surface. The transparency of the ionomer of this  
21 invention allows visual inspection of the surface of the  
22 wrapped product, permitting a customer to inspect a product  
23 for flaws prior to receipt and unwrapping of the product.

24 Ionomer of this invention can also be used as a glass inter-  
25 layer. The ionomer provides shatter resistance, sound  
26 dampening, and/or bullet-proof characteristics to the glass  
27 structure incorporating the ionomer.

28 Single-layer ionomer film or multi-layer film containing  
29 ionomer of this invention can be used to make easy-open  
30 packaging such as easy-tear film, bags, pouches and parcels.  
31 A tear propagates linearly through the film, both in the  
32 machine and transverse directions in blown and cast films,

1 and the Elmendorf tear strength of the ionomer indicates  
2 that it is well-suited to uses such as easy-opening  
3 packaging. The package in which the film is incorporated  
4 normally is notched or incorporates a tear strip to  
5 facilitate ease of opening of the package.

6 The ionomer of this invention can also serve as its own tie  
7 layer due to its good adhesion to other layers. This  
8 eliminates the need for separate tie layers in a multi-layer  
9 film, reducing the thickness of the multi-layer film and  
10 reducing the overall cost of making the multi-layer film.

11 Ionomer of this invention can be blended with other polymers  
12 to modify the properties of the ionomer and/or the polymer  
13 with which it is blended. Ionomer of this invention forms  
14 compatible blends with many polymers. The ionomer can  
15 improve processability of polymers such as ethylene-vinyl  
16 alcohol copolymer and polyesters. Ionomer can be used to  
17 adjust many properties of the blended composition, such as  
18 the elasticity, impact resistance, amount of shrinkage of  
19 polymer used in injection-molding, softness, flexibility,  
20 heat seal, hot tack, and brittleness, and can be used in  
21 those applications where ionomer alone is used.

22 The ionomer of this invention can also be used alone or in  
23 combination with other polymers to make peelable seals.

24 Polymers with which the ionomer of this invention may be  
25 blended include ethylene-acrylic acid and -methacrylic acid  
26 copolymers; other ionomers such as ethylene-acrylic acid and  
27 -methacrylic acid ionomers partially neutralized with  
28 sodium, zinc, lithium, and/or other cations; ethylene alkyl  
29 acrylate and methacrylate copolymers, including ethylene-  
30 methyl acrylate copolymer, ethylene-methyl methacrylate  
31 copolymer, ethylene-ethyl acrylate copolymer and ethylene-

1 butyl acrylate copolymer; ethylene-vinyl acetate copolymer;  
2 polyolefins, including low, linear low, medium and high-  
3 density polyethylene, polypropylene, and polybutadiene;  
4 ethylene vinyl alcohol copolymer; polyamides, including  
5 nylon 6, nylon 12 and nylon 6,6; polyesters, including  
6 poly(ethylene terephthalate); polycarbonates; polystyrene,  
7 including high-impact polystyrene, acrylonitrile-butadiene-  
8 styrene copolymer, and block copolymers of styrene and  
9 butadiene; poly(vinyl chloride); polyurethane; and epoxy  
10 resins.

11 Ionomer of this invention blends well with ethylene alkyl  
12 acrylate and/or methacrylate copolymers. The ionomer and  
13 copolymer form compatible blends, where there is little or  
14 no phase separation. Blending permits tailoring the heat  
15 seal and hot tack properties for particular uses.

16 Ionomer of this invention may also be cross-linked to other  
17 polymers that have reactive groups. Cross-linking can be  
18 achieved by irradiation, by organic peroxide-induced cross-  
19 linking, or via acidolysis or transesterification. In this  
20 manner, properties such as melt-point temperature,  
21 processability, elasticity, impact resistance, amount of  
22 shrinkage of polymer used in injection-molding, softness,  
23 flexibility, heat seal, hot tack, and brittleness may be  
24 further modified. A polymer having a reactive group is one  
25 typically formed by reacting bi- or tri- or multi-functional  
26 monomers to form polymers having at least one functional  
27 (i.e. reactive) group on the side and/or end of the polymer  
28 backbone. The reactive group is one that is capable of  
29 participating in an acidolysis or a transesterification  
30 reaction.

31 Examples of polymers with which ionomer of this invention  
32 may be cross-linked through reactive groups via acidolysis

1 include polyesters, such as poly(ethylene terephthalate),  
2 polyamides, such as nylon 6 and nylon 6,6, polyurethanes,  
3 and polycarbonates. In these polymers, the functional or  
4 reactive group is an amine or a carboxyl group. Examples of  
5 polymers with which ionomer of this invention may be cross-  
6 linked through a reactive group via transesterification  
7 include polyesters and ethylene-alkyl acrylate and  
8 -methacrylate copolymers. In these polymers, the functional  
9 or reactive group is a carboxyl group or an ester.

10 Cross-linking may occur in any equipment suitable to acidify  
11 or transesterify the polymers. A twin-screw reactive  
12 extruder can be used to form a melt blend of the ionomer and  
13 polymer with which the ionomer will be linked and to perform  
14 the acidification or transesterification. The acid or  
15 transesterification catalyst may be fed to the extruder with  
16 the ionomer and polymer to which the ionomer is to be  
17 linked, and/or the acid or transesterification catalyst may  
18 be fed directly to a reaction zone of the reactive extruder.  
19 Many acids may be used in the acidification reaction, but  
20 preferably the acid is a weak organic acid such as carbonic  
21 or acetic acid. Any transesterification catalyst may be  
22 used, but preferably the catalyst is a titanate such as  
23 tetraethyl titanate. A reactive extruder typically has a  
24 devolatilization section to remove volatile byproducts of  
25 acidification or transesterification, and if desired, the  
26 reacted blend may also be treated with a high pH compound  
27 such as sodium hydroxide or soda ash to remove any excess  
28 acidity after acidification. The properties of a blend of  
29 ionomer and other polymers can thus be further modified by  
30 cross-linking the blend.

31 Ionomer compositions of this invention may also be used in  
32 thermally extruded and thermally formed products such as  
33 automotive interior parts and skin packaging. The ionomer

1 compositions may be used alone or in combination with other  
2 polymers in blow-molded or injection molded articles,  
3 particularly where such articles need to be grease- and oil-  
4 resistant such as bottles for fragrances or detergents, and  
5 the compositions may also be used in articles such as food  
6 trays formed by vacuum thermo-forming. The ionomer  
7 compositions of this invention may be used in making  
8 articles such as golf ball covers; coated fabrics;  
9 orthopedic, prosthetic and medical devices; recreational  
10 equipment; and footwear components. The ionomer  
11 compositions of this invention are especially useful in  
12 applications where the ionomer properties discussed above,  
13 as well as the excellent abrasion resistance, transparency,  
14 and/or directional tear properties of the ionomer, are  
15 useful.

16 Theories discussed herein are intended to provide possible  
17 explanations for what was observed. These theories are not  
18 to be interpreted as limiting the invention described  
19 herein. Also, the following examples are illustrative and  
20 are not intended to limit the invention disclosed herein.

#### 21 EXAMPLE 1

22 An ethylene-methyl acrylate copolymer (manufactured by  
23 Chevron by the method disclosed in U.S. Patent  
24 No. 3,350,372) containing 20% by weight methyl acrylate  
25 (7.5 mole %) and having a melt index of 400 g/10 min.  
26 (190°C) was fed to a Werner & Pfleiderer corrosion-resistant  
27 ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. The  
28 extruder had a ratio of length to diameter of about 44. The  
29 screw configuration for Examples 1-13 and Comparative  
30 Example A is given in Table 1 column A. Aqueous sodium  
31 hydroxide (50% NaOH by weight in all examples, except where  
32 noted otherwise) was fed to Zone 3 of the extruder at  
33 9.3 lbs./hr. The screw speed was 550 rpm.

1 The following extruder temperatures were measured:

2 Table 2

3 Zone No.	1	2	3	4	5	6	7
4 Temperature 5 (°C)	236	350	253	253	230	245	260

6 Note: Zone 1: melting section for polymer to be reacted;  
7 Zone 2 & 3: reaction section;  
8 Zone 4: devolatilization section;  
9 Zones 5-7: extrusion section.

10 Water from the sodium hydroxide solution and the reaction  
11 by-product methanol were removed by a two-stage  
12 devolatilization. In all examples, the evolved water and  
13 methanol from the first devolatilization stage were  
14 condensed at atmospheric pressure. The second  
15 devolatilization stage was connected to a vacuum system in  
16 all examples. The second devolatilization stage had 28.4  
17 in. Hg vacuum during this run.

18 The reaction product was extruded through an eight-strand  
19 die, cooled on a stainless steel belt (about 20 feet in  
20 length, made by Sandvik) which was chilled by cold water  
21 underneath the belt, and subsequently pelletized.

22 The product had a melt flow rate of 0.33 g/10 min. (230°C).  
23 The product had a hydrolysis of 53% (i.e., 53% of the methyl  
24 acrylate in the ethylene-methyl acrylate copolymer was  
25 converted to sodium acrylate).

26 The polymer was made into blown film on a Victor blown film  
27 line at the following processing conditions:

Table 3

Zone 1	Zone 2	Zone 3	Adapter	Die 1	Die 2	Die Pressure	Melt Temperature
400°F	440°F	515°F	435°F	430°F	440°F	7600 psi	440°F

The blown film had a thickness of 3.5 mils. The haze of the film was 2%, and the 60° gloss was 122. The 1% secant moduli of the film were 12,740 and 10,080 psi respectively for the machine direction (MD) and the transverse direction (TD).

All haze values were measured using the method of ASTM D 1003. The 60° gloss values were measured using the method of ASTM D 2457. The 1% secant modulus values and tensile strength values were measured using the method of ASTM D-638.

Melt index of feed resin was measured by the method of ASTM D 1239, using a temperature of 190°C and a 2.16 kg weight. The melt flow rate of a composition of this invention was determined by the method of ASTM D 1239 but using a temperature of 230°C rather than 190°C and using a 2.16 kg weight.

The hydrolysis of the product is defined as the moles of metal salt of the alpha, beta-ethylenically-unsaturated carboxylic acid present in the product, expressed as a percentage of the moles of the ester of alpha, beta-ethylenically-unsaturated carboxylic acid present prior to saponifying the copolymer. The terms "hydrolysis", "extent of hydrolysis", "percent hydrolysis", "percent saponified", and "extent of saponification" are used interchangeably.

1 The extent of hydrolysis is determined by dissolving 10 g.  
2 of ionomer in 250 ml. of tetrahydrofuran (THF) in a 500 ml.  
3 round-bottom flask, to which 1 ml. of glacial acetic acid is  
4 added. The flask is fitted with a refluxing condenser, and  
5 the contents are boiled for about 20 min. The mixture is  
6 poured into 1 liter of cold distilled water (about 15-20°C),  
7 and then filtered. The precipitate is subsequently washed  
8 with about 3 liters of distilled water. The precipitate is  
9 dried under vacuum, then weighed and dissolved in THF and  
10 titrated with 0.1 N potassium hydroxide in ethanol, using  
11 thymol blue to indicate the end-point of titration. The  
12 extent of hydrolysis is then calculated by dividing the  
13 moles of potassium used in titrating the sample by the moles  
14 of ester present in the initial ethylene-methyl acrylate  
15 copolymer prior to the saponification reaction.

#### 16 EXAMPLE 2

17 The ethylene-methyl acrylate copolymer of Example 1 was fed  
18 to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin  
19 screw extruder at a rate of 100 lbs./hr. Aqueous sodium  
20 hydroxide was fed to Zone 3 of the extruder at a rate of  
21 11.2 lbs./hr. The screw speed was 500 rpm.

22 The following temperatures were measured during the process:

23 Table 4

24 Zone No.	1	2	3	4	5	6	7
25 Temperature 26 (°C)	271	252	255	256	230	231	241

27 The vacuum on the second devolatilization zone was 28.4 in.  
28 Hg. The reaction product was extruded, cooled on a Sandvik  
29 belt and pelletized in the same way as Example 1. The  
30 product had a melt flow rate of 0.20 g/10 min. (230°C). The  
31 hydrolysis of the product was 65%.

1 The polymer was made into blown film on a Victor blown film  
2 line using the processing conditions similar to those in  
3 Example 1. The haze of the blown film was 2%, and the 60°  
4 gloss was 133. The film had a tensile strength of 4010 and  
5 3180 psi respectively for MD and TD. The 1% secant moduli  
6 of the film were 14720 and 13110 psi respectively for MD and  
7 TD.

8 EXAMPLE 3

9 The ethylene-methyl acrylate copolymer of Example 1 was fed  
10 to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin  
11 screw extruder at a rate of 100 lbs./hr. Aqueous sodium  
12 hydroxide was fed to Zone 3 on the extruder at a rate of  
13 12.1 lbs./hr. The screw speed was 500 rpm.

14 The following temperatures were measured during the process:

15 Table 5

16 Zone No.	1	2	3	4	5	6	7
17 Temperature 18 (°C)	218	347	255	255	230	251	260

19 The vacuum on the second devolatilization zone was 28.5 in.  
20 Hg. The reaction product was extruded, cooled on a Sandvik  
21 belt and pelletized in the same way as Example 1. The  
22 product had a melt flow rate of 0.1 g/10 min. (230°C). The  
23 hydrolysis of the product was 70%.

24 The polymer was made into blown film on a Victor blown film  
25 line using the processing conditions similar to those in  
26 Example 1. The haze of the blown film was 2%, and the 60°  
27 gloss was 134. The film had a tensile strength of 4470 and  
28 2420 psi respectively for MD and TD.

EXAMPLE 4

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 570 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3 on the extruder at a rate of 13.0 lbs./hr. The screw speed was 500 rpm.

The following temperatures were measured during the process:

Table 6

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	178	242	254	252	301	303	289

The vacuum on the second devolatilization zone was 25.5 in. Hg. The reaction product was extruded, cooled on a Sandvik belt and pelletized in the same way as Example 1. The product had a melt flow rate of 0.87 g/10 min. (230°C). The hydrolysis of the product was 69%.

The polymer was made into blown film on a Victor blown film line using the processing conditions similar to those in Example 1. The haze of the blown film was 2%, and the 60° gloss (ASTM D 2457) was 135. The film had a tensile strength of 2870 and 1760 psi respectively for MD and TD.

EXAMPLE 5

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 440 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3

1 on the extruder at a rate of 13.0 lbs./hr. The screw speed  
2 was 500 rpm.

3 The following temperatures were measured during the process:

4 Table 7

5 Zone No.	1	2	3	4	5	6	7
6 Temperature 7 (°C)	189	257	257	258	251	263	283

8 The vacuum on the second devolatilization zone was 28.4 in.  
9 Hg. The reaction product was extruded, cooled on a Sandvik  
10 belt and pelletized in the same way as Example 1. The  
11 product had a melt flow rate of 0.81 g/10 min. (230°C). The  
12 hydrolysis of the product was 72%.

13 The polymer was made into blown film on a Victor blown film  
14 line using the processing conditions similar to those in  
15 Example 1. The haze of the blown film was 2%, and the 60°  
16 gloss was 135. The film had a tensile strength of 2600 and  
17 1850 psi respectively for MD and TD.

18 EXAMPLE 6

19 An ethylene-methyl acrylate copolymer containing 23% by  
20 weight methyl acrylate and having a melt index of  
21 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer  
22 corrosion-resistant ZSK-40mm twin screw extruder at a rate  
23 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3  
24 on the extruder at a rate of 10.7 lbs./hr. The screw speed  
25 was 500 rpm.

1 The following temperatures were measured during the process:

Table 8

2 Zone No.	1	2	3	4	5	6	7
3 Temperature	181	247	256	255	255	254	270
4 (°C)							

5  
6 The vacuum on the second devolatilization zone was 26.7 in.  
7 Hg. The reaction product was extruded, cooled on a Sandvik  
8 belt and pelletized in the same way as Example 1. The  
9 product had a melt flow rate of 0.54 g/10 min. (230°C). The  
10 hydrolysis of the product was 51%.

11 The polymer was made into blown film on a Victor blown film  
12 line using the processing conditions similar to those in  
13 Example 1. The haze of the blown film was 2%, and the 60°  
14 gloss was 124. The film had a tensile strength of 2270 and  
15 1470 psi respectively for MD and TD.

#### 16 EXAMPLE 7

17 An ethylene-methyl acrylate copolymer containing 23% by  
18 weight methyl acrylate and having a melt index of  
19 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer  
20 corrosion-resistant ZSK-40mm twin screw extruder at a rate  
21 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3  
22 on the extruder at a rate of 12.8 lbs./hr. The screw speed  
23 was 500 rpm.

24 The following temperatures were measured during the process:

Table 9

25 Zone No.	1	2	3	4	5	6	7
26 Temperature	175	247	253	259	254	257	271
27 (°C)							

1 The vacuum on the second devolatilization zone was 26.6 in.  
2 Hg. The reaction product was extruded, cooled on a Sandvik  
3 belt and pelletized in the same way as Example 1. The  
4 product had a melt flow rate of 0.45 g/10 min. (230°C). The  
5 hydrolysis of the product was 61%.

6 The polymer was made into blown film on a Victor blown film  
7 line using the processing conditions similar to those in  
8 Example 1. The haze of the blown film was 3%, and the 60°  
9 gloss was 132. The film had a tensile strength of 2730 and  
10 1960 psi respectively for MD and TD.

11 EXAMPLE 8

12 An ethylene-methyl acrylate copolymer containing 23% by  
13 weight methyl acrylate and having a melt index of  
14 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer  
15 corrosion-resistant ZSK-40mm twin screw extruder at a rate  
16 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3  
17 on the extruder at a rate of 9.6 lbs./hr. The screw speed  
18 was 500 rpm.

19 The following temperatures were measured during the process:

20 Table 10

21 Zone No.	1	2	3	4	5	6	7
22 Temperature	193	284	257	259	254	254	271
23 (°C)							

24 The vacuum on the second devolatilization zone was 26.2 in.  
25 Hg. The reaction product was extruded, cooled on a Sandvik  
26 belt and pelletized in the same way as Example 1. The  
27 product had a melt flow rate of 0.60 g/10 min. (230°C). The  
28 hydrolysis of the product was 46%.

1 The polymer was made into blown film on a Victor blown film  
2 line using the processing conditions similar to those in  
3 Example 1. The haze of the blown film was 2%, and the 60°  
4 gloss was 120. The film had a tensile strength of 1950 and  
5 1240 psi respectively for MD and TD.

6 EXAMPLE 9

7 An ethylene-methyl acrylate copolymer containing 22% by  
8 weight methyl acrylate and having a melt index of  
9 470 g/10 min. (190°C) was fed to the Werner & Pfleiderer  
10 corrosion-resistant ZSK-40mm twin screw extruder at a rate  
11 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3  
12 on the extruder at a rate of 14.3 lbs./hr. The screw speed  
13 was 500 rpm.

14 The following temperatures were measured during the process:

15 Table 11

16 Zone No.	1	2	3	4	5	6	7
17 Temperature 18 (°C)	298	326	255	266	254	254	271

19 The vacuum on the second devolatilization zone was 28.4 in.  
20 Hg. The reaction product was extruded, cooled on a Sandvik  
21 belt and pelletized in the same way as Example 1. The  
22 product had a melt flow rate of 0.23 g/10 min. (230°C). The  
23 hydrolysis of the product was 70%.

24 The polymer was made into blown film on a Victor blown film  
25 line using the processing conditions similar to those in  
26 Example 1. The haze of the blown film was 1%, and the 60°  
27 gloss was 134. The film had a tensile strength of 3000 and  
28 2170 psi respectively for MD and TD.

**EXAMPLE 10**

An ethylene-methyl acrylate copolymer containing 23% by weight methyl acrylate and having a melt index of 500 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3 on the extruder at a rate of 8.6 lbs./hr. The screw speed was 500 rpm.

The following temperatures were measured during the process:

Table 12

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	177	262	255	253	254	255	270

The vacuum on the second devolatilization zone was 25.8 in. Hg. The reaction product was extruded, cooled on a Sandvik belt and pelletized in the same way as Example 1. The product had a melt flow rate of 1.25 g/10 min. (230°C). The hydrolysis of the product was 41%.

The polymer was made into blown film on a Victor blown film line using the processing conditions similar to those in Example 1. The haze of the blown film was 4%, and the 60° gloss was 104. The film had a tensile strength of 1910 and 970 psi respectively for MD and TD.

**EXAMPLE 11**

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 100 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3

1 on the extruder at a rate of 4.7 lbs./hr. The screw speed  
2 was 500 rpm.

3 The following temperatures were measured during the process:

Table 13

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	253	322	254	230	230	231	241

8 The vacuum on the second devolatilization zone was 28.4 in.  
9 Hg. The reaction product was extruded, cooled on a Sandvik  
10 belt and pelletized in the same way as Example 1. The  
11 product had a melt flow rate of 0.67 g/10 min. (230°C). The  
12 hydrolysis of the product was 26%.

13 The polymer was made into blown film on a Victor blown film  
14 line using the processing conditions similar to those in  
15 Example 1. The haze of the blown film was 3%, and the 60°  
16 gloss was 115. The film had a tensile strength of 1150 and  
17 1080 psi respectively for MD and TD.

#### EXAMPLE 12

18 An ethylene-methyl acrylate copolymer containing 20% by  
19 weight methyl acrylate and having a melt index of  
20 400 g/10 min. (190°C) was fed to the Werner & Pfleiderer  
21 corrosion-resistant ZSK-40mm twin screw extruder at a rate  
22 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3  
23 on the extruder at a rate of 9.3 lbs./hr. The screw speed  
24 was 500 rpm.  
25

1 The following temperatures were measured during the process:

2 Table 14

3 Zone No.	1	2	3	4	5	6	7
4 Temperature 5 (°C)	209	201	266	255	256	256	256

6 The vacuum on the second devolatilization zone was 24.7 in.  
7 Hg. The reaction product was extruded, cooled in a water  
8 bath, and pelletized. The pellets were dried in a vacuum  
9 over at 65°C and 29.5 in. Hg for 48 hours. The product had  
10 a melt flow rate of 0.66 g/10 min. (230°C). The hydrolysis  
11 of the product was 49%.

12 The polymer was made into blown film on a Victor blown film  
13 line using the processing conditions similar to those in  
14 Example 1. The haze of the blown film was 3%, and the 60°  
15 gloss was 128.

16 EXAMPLE 13

17 An ethylene-methyl acrylate copolymer containing 20% by  
18 weight methyl acrylate and having a melt index of  
19 150 g/10 min. (190°C) was fed to the Werner & Pfleiderer  
20 corrosion-resistant ZSK-40mm twin screw extruder at a rate  
21 of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3  
22 on the extruder at a rate of 7.4 lbs./hr. The screw speed  
23 was 450 rpm.

24 The following temperatures were measured during the process:

25 Table 15

26 Zone No.	1	2	3	4	5	6	7
27 Temperature 28 (°C)	188	199	276	253	257	260	262

1 The vacuum on the second devolatilization zone was 28.5 in.  
2 Hg. The reaction product was extruded, cooled in a water  
3 bath, and pelletized. The pellets were dried in a vacuum  
4 over at 65°C and 29.5 in. Hg for 48 hours. The product had  
5 a melt flow rate of 0.22 g/10 min. (230°C). The hydrolysis  
6 of the product was 42%.

7 The polymer was made into blown film on a Victor blown film  
8 line using the processing conditions similar to those in  
9 Example 1. The haze of the blown film was 4%, and the 60°  
10 gloss was 122.

#### 11 EXAMPLE 14

12 An ethylene-methyl acrylate copolymer containing 20% by  
13 weight methyl acrylate and having a melt index of  
14 400 g/10 min. (190°C) was fed to a Werner & Pfleiderer  
15 ZSK-58mm twin screw extruder at a rate of 425 lbs./hr. The  
16 screw was configured to provide substantially the same  
17 mixing as provided in the ZSK-40mm extruder in Examples 1-  
18 13. Aqueous sodium hydroxide was fed to the reaction zone  
19 on the extruder at a rate of 56 lbs./hr.

20 The screw speed of the extruder was at 500 rpm. The  
21 temperatures in the reaction zones were 226°C to 338°C. The  
22 product was 71% hydrolyzed. The product had similar optical  
23 properties to the product of Example 3.

#### 24 EXAMPLE 15

25 An ethylene-methyl acrylate copolymer containing 20% by  
26 weight methyl acrylate and having a melt index of  
27 400 g/10 min. (190°C) was fed to a Werner & Pfleiderer  
28 ZSK-70mm twin screw extruder at a rate of 450 lbs./hr. The  
29 screw was configured to provide substantially the same  
30 mixing as provided in the ZSK-40mm extruder in Examples 1-

13. Aqueous sodium hydroxide was fed to the reaction zone on the extruder at a rate of 50 lbs./hr.

The screw speed of the extruder was at 580 rpm. The temperatures in the reaction zones were 330°C to 350°C. The product was 61% hydrolyzed. The product had similar optical properties to the product of Example 3.

#### COMPARATIVE EXAMPLE A

An ethylene-methyl acrylate copolymer containing 20% by weight methyl acrylate and having a melt index of 20 g/10 min. (190°C) was fed to the Werner & Pfleiderer corrosion-resistant ZSK-40mm twin screw extruder at a rate of 100 lbs./hr. Aqueous sodium hydroxide was fed to Zone 3 on the extruder at a rate of 4.6 lbs./hr. The screw speed was 400 rpm.

The following temperatures were measured during the process:

Table 16

Zone No.	1	2	3	4	5	6	7
Temperature (°C)	216	213	270	269	270	271	270

The vacuum on the second devolatilization zone was 27.9 in. Hg. The reaction product was extruded, cooled in a water bath, and pelletized. The pellets were dried in a vacuum oven at 65°C and 29.5 in. Hg for 48 hours. The product had a melt flow rate of 3.2 g/10 min. (190°C). The hydrolysis of the product was 15%.

The polymer was made into blown film on a Victor blown film line using the processing conditions similar to those in Example 1. The haze of the blown film was 81%, and the 60° gloss was 35.

1 This Comparative Example A shows that saponifying 15% of the  
2 methyl acrylate groups to form the sodium salt of acrylic  
3 acid is insufficient at these reaction conditions to produce  
4 the low haze of compositions of this invention.

5 COMPARATIVE EXAMPLE B

6 An ethylene-methyl acrylate copolymer containing 20% methyl  
7 acrylate by weight and having a melt index of 400 g/10 min.  
8 was fed to a Werner & Pfleiderer ZSK-30 corrosion-resistant  
9 extruder at 13.2 lbs/hr. 1.73 lbs/hr. of 35% sodium  
10 hydroxide solution was fed to zone 3 of the extruder. The  
11 extruder had the configuration of elements shown in Table 1  
12 column B.

13 The following extruder temperatures were measured:

14 Table 17

15 Zone No.	1	2	3	4	5	6	7
16 Temperature 17 (°C)	230	275	275	275	275	240	235

18 Water and the by-product methanol were removed in a two-  
19 stage devolatilization zone. The polymer strands were  
20 cooled in a water bath and pelletized. The pellets were  
21 vacuum-dried overnight at about 25 in. Hg vacuum and at  
22 68°C.

23 Chemical analysis of the product indicated a degree of  
24 saponification of 49.2%. The product had a melt index  
25 (190°C) of 0.54 g/10 min.

26 A 1/2 inch Randcastle miniextruder was used to make a cast  
27 film of about 4 inch width. The temperature at the feed  
28 zone and barrels 1A through 3A was 430°C, while the die

1 temperature was 440°C. The film had a haze of 55% and a 60°  
2 gloss of 20.

3 It is believed that the poor clarity of this example results  
4 from a more dilute caustic solution and poorer mixing at  
5 these reaction conditions as compared to the conditions  
6 which produce compositions of this invention.

#### 7 COMPARATIVE EXAMPLE C

8 An ethylene-methyl acrylate copolymer containing 20% methyl  
9 acrylate by weight and having a melt index of 400 g/10 min.  
10 was fed to a Werner & Pfleiderer ZSK-30 corrosion-resistant  
11 extruder at 13.2 lbs/hr. 2.29 lbs/hr. of 35% sodium  
12 hydroxide solution was fed to zone 3 of the extruder. The  
13 extruder had the configuration of elements shown in Table 1  
14 column B.

15 The following extruder temperatures were measured:

16 Table 18

17 Zone No.	1	2	3	4	5	6	7
18 Temperature 19 (°C)	230	275	275	275	275	240	235

20 Water and the by-product methanol were removed in a two-  
21 stage devolatilization zone. The polymer strands were  
22 cooled in a water bath and pelletized. The pellets were  
23 vacuum-dried overnight at about 25 in. Hg vacuum and at  
24 68°C.

25 Chemical analysis of the product indicated a degree of  
26 saponification of 65.2%. The product had a melt flow rate  
27 of 0.38 g/10 min. (230°C).

1 A 1/2 inch Randcastle miniextruder was used to make a cast  
2 film of about 4 inch width. The temperature at the feed  
3 zone and barrels 1A through 3A was 430°C, while the die  
4 temperature was 440°C. The film had a haze of 15% and a 60°  
5 gloss of 66.

6 This comparative example shows that a greater extent of  
7 hydrolysis provided clearer ionomer, but mixing conditions  
8 as supplied by the screw design of Table 1 column B when  
9 using 35% aqueous caustic did not appear to provide the  
10 intensive mixing and reaction conditions necessary to obtain  
11 a haze of 10% or less.

#### 12 COMPARATIVE EXAMPLE D

13 Ethylene-methyl acrylate copolymer having 20 weight percent  
14 methyl acrylate and a 400 melt index (190°C) was saponified  
15 with a 35% by weight aqueous solution of sodium hydroxide  
16 per the method of Comparative Example B. The product was  
17 60% saponified and had a melt index (190°C) of 0.06. The  
18 tensile strength in the machine direction was 1582 psi.

#### 19 COMPARATIVE EXAMPLE E

20 Ethylene-methyl acrylate copolymer having 25 weight percent  
21 methyl acrylate and a 457 melt index (190°C) was saponified  
22 with a 35% by weight aqueous solution of sodium hydroxide  
23 per the method of Comparative Example B. The product was  
24 44% saponified and had a melt index (190°C) of 0.04. The  
25 tensile strength in the machine direction was 985 psi.

#### 26 EXAMPLE 16 -- ACID BATH COOLING OF IONOMER

27 26.4 lbs./hr. of the ethylene-methyl acrylate copolymer of  
28 Example 1 were fed to a Werner & Pfleiderer corrosion  
29 resistant ZSK-30 twin-screw extruder having the  
30 configuration of elements given in Table 1 column C. 50%

1 aqueous sodium hydroxide was fed into zone 3 at 2.5 lb./hr.  
2 The screw speed was 500 rpm.

3 The following extruder temperatures were measured:

4 Table 19

5 Zone No.	1	2	3	4	5	6	7
6 Temperature 7 (°C)	174	200	255	260	254	267	255

8 Volatile components were removed in a two port  
9 devolatilization section, and the second port had a vacuum  
10 of 28 in. Hg. The polymer strands from a four-strand die  
11 were cooled in a 5% phosphoric acid bath which was 10 ft.  
12 long, and were then rinsed in a 2 ft. water bath and  
13 pelletized in a Conair pelletizer.

14 During 1.75 hours of operation, the ionomer was efficiently  
15 cooled and pelletized, and the acid bath remained acidic and  
16 clear with no evidence of dissolved polymer. Total carbon  
17 analysis of the cooling water (determined by potentiometric  
18 titration) at the end of operation showed less than 20 ppm  
19 of dissolved carbon. By contrast, when the same polymer was  
20 cooled in water, the water bath became turbid and milky-  
21 white within a few minutes of operation.

22 The resulting pellets were colorless, shiny, and clear.

23 EXAMPLE 17

24 This example shows a copolymer of ethylene, methyl acrylate,  
25 sodium acrylate, and acrylic acid. First, ethylene-methyl  
26 acrylate copolymer having 20 weight percent methyl acrylate  
27 and 153 melt index (190°C) was saponified in a Werner-  
28 Pfeleiderer ZSK-30 twin-screw reactive extruder using 50%  
29 aqueous sodium hydroxide and substantially the same reaction

1 conditions as Example 16. The extent of saponification was  
2 42%. The pelletized ionomer was clear and glossy and had a  
3 melt flow rate (230°C) of 0.17 g/10 min.

4 The ionomer pellets were fed to the extruder at a rate of 12  
5 kg/hr. 85.6% aqueous phosphoric acid was fed to Zone 3 of  
6 the extruder at a rate of 0.14 kg/hr., and the product was  
7 extruded, cooled in a water bath, and pelletized.

8 The product retained its clear and glossy optical  
9 properties, and the melt flow rate increased to 1.0 g/10  
10 min. (230°C). Film that was made on the Randcastle mini-  
11 extruder had a tensile strength in the machine direction of  
12 2418 psi.

#### 13 EXAMPLE 18

14 Ethylene-methyl acrylate copolymer having 20 weight percent  
15 methyl acrylate and 400 melt index (190°C) was saponified in  
16 a ZSK-30 extruder having the configuration of elements given  
17 in Table 1 column C with 50% aqueous sodium hydroxide at a  
18 reaction temperature of about 148°C. The screw speed was  
19 500 rpm. The copolymer was fed to the extruder at a rate of  
20 12 kg/hr., and the product was about 54% saponified. The  
21 product was visually clear.

#### 22 COMPARATIVE EXAMPLE F

23 Ethylene-methyl acrylate copolymer having 20 weight percent  
24 methyl acrylate and 400 melt index (190°C) was saponified  
25 with 50% aqueous sodium hydroxide in a ZSK-30 extruder  
26 having the configuration of screw elements given in Table 1  
27 column B at a reaction temperature of about 149°C. The  
28 screw speed was 500 rpm. The copolymer was fed to the  
29 extruder at a rate of 16 kg/hr., and the product was about  
30 52% saponified. The product was visually cloudy.

1 This example shows that insufficient mixing was supplied by  
2 the screw configuration of Table 1 column B at these  
3 reaction conditions.

#### 4 EXAMPLE 19

5 26.4 lbs./hr. of the ethylene-methyl acrylate copolymer of  
6 Example 1 were fed to a Werner & Pfleiderer corrosion  
7 resistant ZSK-30 twin-screw extruder having the  
8 configuration of elements given in Table 1 column C. 50%  
9 aqueous potassium hydroxide was fed into zone 3 at the rate  
10 given in Table 20. The screw speed was 500 rpm.

11 The extruder temperatures were substantially the same as  
12 those given in Table 19. Volatile components were removed  
13 in a two port devolatilization section, and the second port  
14 had a vacuum of 28 in. Hg. The following table summarizes  
15 the feed rate of potassium hydroxide, the melt flow rate  
16 (230°C), and the extent of saponification of the methyl  
17 acrylate groups.

18 TABLE 20

19 Feed rate 20 (lb./hr.) of 50% 21 aqueous potassium 22 hydroxide	Melt flow rate of ionomer of this Example	Extent of saponification
23 1.87	1.66	27
24 2.62	0.60	37
25 3.74	0.23	53
26 5.28	0.07	78

#### 27 COMPARATIVE EXAMPLE G

28 An ethylene-methyl acrylate copolymer containing 20% methyl  
29 acrylate by weight and having a melt index of 20 g/10 min.  
30 (190°C) was fed to a Werner & Pfleiderer ZSK-40 corrosion-  
31 resistant extruder at 100 lbs/hr. 4.7 lbs/hr. of 50% sodium

1 hydroxide solution was fed to zone 3 of the extruder. The  
2 screw speed was 275 rpm.

3 The following extruder temperatures were measured:

4 Table 21

5 Zone No.	1	2	3	4	5	6	7
6 Temperature 7 (°C)	200	208	279	280	278	280	281

8 The vacuum on the second devolatilization zone was 27.0 in.  
9 Hg. The reaction product was extruded, cooled in a water  
10 bath, and pelletized. The pellets were dried in a vacuum  
11 oven at 65°C and 29.5 in. Hg for 48 hours. The product had  
12 a melt index of 1.6 g/10 min. (190°C). The hydrolysis of  
13 the product was 24%.

14 The polymer was made into blown film on a Victor blown film  
15 line using the processing conditions similar to those in  
16 Example 1. The haze of the blown film was 97%, and the 60°  
17 gloss was 43.

18 The SEM micrograph shown in Figure 2 was taken on a freeze-  
19 fractured surface of the blown film made from this ionomer.

#### 20 COMPARATIVE EXAMPLE H

21 An ethylene-methyl acrylate copolymer having 20 weight  
22 percent methyl acrylate and a melt index of 153 g/10 min.  
23 (190°C) was 35% hydrolyzed by the method of Comparative  
24 Example A. The melt index of this ionomer was 9.7 g/10 min.  
25 (190°C), and the haze of a cast film was 98%, the 60° gloss  
26 was 6, and the tear strength (g/mil) in the machine  
27 direction was 33 and in the transverse direction was 41.

EXAMPLE 20

- 1
- 2     An ethylene-methyl acrylate copolymer having 20 weight
- 3     percent methyl acrylate was saponified substantially by the
- 4     method of Example 1. The percent hydrolysis and properties
- 5     of the polymer are listed in the following Table 22.

TABLE 22

% HYDRO- LYZED	% HAZE	60° GLOSS	TENSILE STRENGTH, psi		1° SECANT MODULUS, psi		MELT POINT TEMP. °C	ELMENDORF TEAR STRENGTH, g/mil		ELONGATION @ BREAK, %	
			MD	TD	MD	TD		MD	TD	MD	TD
35	13.3	55	1709	1445	7893	7667	77	12	14	350	376
42	1.4	126	2081	1928	14831	14054	76	17	24	420	434
50	0.5	140	2321	1984	8193	7718	73	26	22	365	405

Melt point temperature was measured using a differential scanning calorimeter and standard methods well-known in the art.  
 Elmendorf tear strength was measured using ASTM D-1922.  
 Elongation at break was measured using ASTM D-882.

1 The hot tack strength for these ionomers is summarized in  
2 Figure 3.

### 3 EXAMPLE 21

4 Samples of ethylene methyl acrylate copolymer having the  
5 methyl acrylate contents in following Table 23 were  
6 saponified to various degrees of hydrolysis using  
7 substantially the method of Example 1. In addition,  
8 ethylene methyl acrylate copolymers made by the method of  
9 U.S. Ser. No. 07/947,870, filed Sep. 21, 1992, where all of  
10 the methyl acrylate was fed to a first reaction zone of a  
11 multi-zone high-pressure polymerization reactor, were  
12 saponified to various degrees of hydrolysis. Table 23  
13 summarizes the melt point temperatures of these ionomers.

14 Table 23

15 16 17 WT. % METHYL ACRYLATE	ETHYLENE METHYL ACRYLATE COPOLYMER MADE BY METHOD OF U.S. 3,350,372		ETHYLENE METHYL ACRYLATE COPOLYMER MADE BY METHOD OF U.S. SER. NO. 07/947,870	
	% HYDROLYZED	MELT POINT TEMP., °C	% HYDROLYZED	MELT POINT TEMP., °C
18 12	62	90	60	97
19 12	86	83	83	99
20 12	--	--	83	98
21 12	100	87	99	93
22 20	--	--	35	92
23 20	47	87	42	91
24 20	51	86	50	91
25 20	61	83	65	92
26 20	72	64	--	--
27 24	42	64	--	--

EXAMPLE 22

1  
2 Ionomer was made substantially by the method of Example 1.  
3 This ionomer was cast coextruded individually with three  
4 polymers on a Randcastle Mini-Extruder to form three 2-layer  
5 films, where each layer was 2 mil thick. Adhesion strength  
6 of the 2-layer films was analyzed using TAPPI Uniform Method  
7 541, "Adhesion to Non-Porous Flexible Substrates", which is  
8 incorporated by reference in its entirety herein.  
9 Ionomer/propylene film (Fina 3275) had an adhesion of 770  
10 g/inch; ionomer/high density polyethylene (Chevron HiD®  
11 9650) could not be separated; and ionomer/nylon (Allied  
12 Chemical's Capron 8350) had an adhesion of 80 g/inch.

13 The heat seal strength of the ionomer/polyethylene film  
14 above is summarized in Figure 4.

EXAMPLE 23

15  
16 Ethylene-methyl acrylate-butyl acrylate copolymer containing  
17 10 weight percent methyl acrylate and 10 weight percent  
18 butyl acrylate is about 50% hydrolyzed substantially by the  
19 method of Example 1. This yields an ethylene-methyl  
20 acrylate-butyl acrylate-sodium acrylate copolymer. It is  
21 expected that the methyl acrylate reacts at a faster rate  
22 than the butyl acrylate, so more methyl acrylate is  
23 converted to the sodium salt than butyl acrylate. This  
24 product is useful in applications where a higher melt-point  
25 temperature is desired, such as films or bags which contact  
26 hot food or liquids.

EXAMPLE 24

27  
28 Ionomer #1, ionomer of this invention having an extent of  
29 saponification of 50%, was formed by saponifying ethylene-  
30 methyl acrylate copolymer having 20 wt.% methyl acrylate  
31 with aqueous sodium hydroxide by substantially the method of  
32 Example 1. Ionomer #2, ionomer of this invention having an

1 extent of saponification of about 83%, was formed by  
2 saponifying ethylene-methyl acrylate copolymer having 12  
3 wt.% methyl acrylate with aqueous sodium hydroxide by  
4 substantially the method of Example 1.

5 These ionomers were melt-blended in an twin-screw extruder.  
6 with polypropylene (PROFAX 6523 polypropylene) or with high-  
7 density polyethylene (Chevron HiD 9607, 6 melt index) in the  
8 weight ratios given in Tables 24-26 below. Mold shrinkage  
9 was determined by forming a tensile bar of ionomer in a mold  
10 and comparing the longitudinal length of the tensile bar to  
11 the mold length after the tensile bar sat for several days.  
12 Notched Izod was determined by ASTM D-256, and Vicat  
13 softening point was determined by ASTM D-1525.

14 Table 24  
15 PROPERTIES OF POLYPROPYLENE BLENDED WITH IONOMER #1

16 PARTS POLYPROPYLENE	0	25	75	100
17 PARTS OF IONOMER #1	100	75	25	0
18 MOLD SHRINKAGE, 19 mil/in.	6	8	20	approx. 24 <sup>1</sup>
20 VICAT SOFTENING 21 POINT, °C	60	71	150	160
22 NOTCHED IZOD, 23 ft-lb/in. at room 24 temperature	7	12	2	0

25 <sup>1</sup> Value estimated from literature

26 This data shows surprisingly little mold shrinkage and  
27 surprisingly improved impact resistance (as measured by  
28 notched Izod) for a blend of ionomer of this invention and  
29 polypropylene when less than about 50% of the blend is  
30 polypropylene.

31 Table 25

1 PROPERTIES OF POLYPROPYLENE BLENDED WITH IONOMER #2

2

3

4

5

6

7

8

9

10

PARTS POLYPROPYLENE	0	25	75	100
PARTS OF IONOMER #2	100	75	25	0
MOLD SHRINKAGE, mil/in.	N/A <sup>2</sup>	11	18	approx. 24 <sup>3</sup>
VICAT SOFTENING POINT, °C	76	150	150	160
NOTCHED IZOD, ft-lb/in. at room temperature	6	7	1	0

11 <sup>2</sup> Not available

12 <sup>3</sup> Value estimated from literature

13 This data shows low mold shrinkage and good impact  
14 resistance for blends containing less than about 50%  
15 polypropylene, and shows surprisingly good Vicat softening  
16 point regardless of the amount of polypropylene present in  
17 the blend.

18 Table 26  
19 PROPERTIES OF HIGH DENSITY POLYETHYLENE BLENDED WITH IONOMER  
20 #1

21

22

23

24

25

26

27

28

29

PARTS POLYETHYLENE	0	25	75	100
PARTS OF IONOMER #1	100	75	25	0
MOLD SHRINKAGE, mil/in.	6	4	22	approx. 24 <sup>4</sup>
VICAT SOFTENING POINT, °C	60	82	113	160
NOTCHED IZOD, ft-lb/in. at room temperature	7	10	5	0

30 <sup>4</sup> Value estimated from literature

31 This data shows surprisingly low mold shrinkage when less  
32 than about 50% high-density polyethylene is blended with  
33 ionomer of this invention, and also shows surprisingly good

1 impact resistance for blends of high-density polyethylene  
2 and ionomer.

### 3 EXAMPLE 25

4 Ethylene-alkyl acrylate copolymer blended with ionomer  
5 Ethylene-methyl acrylate copolymer having 16 wt.% methyl  
6 acrylate was made by the method of U.S. Ser. No. 947,870 by  
7 feeding all of the methyl acrylate to a first reaction zone.  
8 Ionomer of this invention was made by saponifying this  
9 copolymer with aqueous sodium hydroxide by substantially the  
10 method of Example 1, so that the resultant copolymer had an  
11 extent of saponification of about 63%. A blend of 10 parts  
12 of ethylene-methyl acrylate copolymer having 20 wt.% methyl  
13 acrylate and 2 melt index and 90 parts of the ionomer was  
14 made by the method of Example 24. Properties listed in  
15 Table 27 were observed:  
16

16 Table 27

	IONOMER OF THIS EXAMPLE	BLEND OF THIS EXAMPLE	ETHYLENE- METHYL ACRYLATE COPOLYMER
17 HAZE, %	0.5	0.6	15
18 60° GLOSS	151	150	70
19 HOT TACK: <sup>5</sup>			
20 80°C	0.13	0.5	1.4 <sup>6</sup>
21 85°C	0.13	1.1	---
22 90°C	0.18	2.2	---
23 95°C	1.7	2.1	---
24 100°C	1.9	2.3	---
25 105°C	2.0	2.4	---
26 110°C	2.0	2.1	---
27 115°C	2.5	2.3	---
28 120°C	2.6	2.4	---
29 125°C	2.2	2.2	---

Also, ethylene methyl acrylate ionomer was made by saponifying ethylene methyl acrylate copolymer having 20 wt. % methyl acrylate and 400 melt index using 50% aqueous NaOH to achieve 50% saponification; this ionomer contained 5% by weight of a low molecular weight ethylene-acrylic acid copolymer, available from Allied Signal as "AC Copolymer" to improve the processability of the ionomer. 5 parts by weight of this ionomer were fed simultaneously with 95 parts of ethylene-methyl acrylate copolymer having 20 wt.% methyl acrylate and a melt index of 2.4 to a preheated screw and extruded into strands. The strands were air-cooled on a 10 foot conveyor belt and pelletized in a Conair pelletizer. The pellets were dried in a vacuum oven at 27 in. Hg and at 67°C for several days. The pelletized blend had a melt index of 1.4 g/10 min.

18 A cast film was made using a Randcastle Miniextruder. The  
19 film was visually clear and mechanically strong. Also, the  
20 heat-seal strength appeared to be very good. Two layers  
21 which had been heat-sealed together could not be pulled  
22 apart by hand easily.

23 This data shows good haze, gloss, heat seal and hot tack for  
24 a blend of ethylene-alkyl acrylate copolymer and ionomer of  
25 this invention.

## 26

## 27

**31**

1 extruder to react the ionomer with terminal amine and/or  
2 carboxyl groups on the nylon. The reacted blend is  
3 devolatilized in a devolatilization section of the reactive  
4 extruder. The resultant polymer is expected to have better  
5 room and low temperature impact resistance and better  
6 scratch resistance.

7 Optionally, melted reacted blend, before or after  
8 devolatilization, is contacted in a second reaction zone  
9 with an amount of 50% aqueous NaOH that is sufficient to  
10 neutralize at least a portion of the acidity on the ionomer  
11 portion of the reacted polymer. This mixture is  
12 devolatilized in a devolatilization zone of a reactive  
13 extruder.

#### 14 EXAMPLE 27

##### 15 Reactive blending of ethylene-methyl acrylate copolymer with 16 ionomer

17 80 parts by weight of ionomer of Example 1 is melt-blended  
18 in a twin-screw reactive extruder with 20 parts by weight of  
19 ethylene-methyl acrylate copolymer having 20 wt.% methyl  
20 acrylate and a melt index of 2. 0.02 part by weight  
21 tetraethyl titanate is added directly to a first reaction  
22 zone of the twin-screw reactive extruder to transesterify  
23 the ionomer and the ethylene-methyl acrylate copolymer. The  
24 reacted blend is devolatilized in a devolatilization section  
25 of the reactive extruder. The resultant polymer is expected  
26 to have improved tear resistance and reduced stiffness.

#### 27 EXAMPLE 28

##### 28 Reactive blending of ethylene-methyl acrylate copolymer with 29 ionomer

30 20 parts by weight of ionomer of Example 1 is melt-blended  
31 in a twin-screw reactive extruder with 80 parts by weight of  
32 ethylene-methyl acrylate copolymer having 20 wt.% methyl

1      acrylate and a melt index of 2. 0.02 part by weight  
2      tetraethyl titanate is added directly to a first reaction  
3      zone of the twin-screw reactive extruder to transesterify  
4      the ionomer and the ethylene-methyl acrylate copolymer. The  
5      reacted blend is devolatilized in a devolatilization section  
6      of the reactive extruder. The resultant polymer is expected  
7      to have increased scratch resistance, greater stiffness, and  
8      improved tensile properties.

1 WE CLAIM:

- 2 1. A composition comprising a copolymer of alpha-olefins  
3 having from two to eight carbon atoms, esters of alpha,  
4 beta-ethylenically-unsaturated carboxylic acids having  
5 from four to twenty-two carbon atoms, and metal salts  
6 of acrylic or methacrylic acid, wherein said copolymer  
7 has a haze of no more than ten percent as measured by  
8 ASTM method D 1003.
- 9 2. The composition of claim 1 having a haze of no more  
10 than seven percent.
- 11 3. The composition of claim 2 having a haze of no more  
12 than five percent.
- 13 4. The composition of claim 3 having a haze of no more  
14 than two percent.
- 15 5. The composition of claim 1 wherein the alpha-olefin  
16 consists essentially of ethylene.
- 17 6. The composition of claim 1 wherein the metal of said  
18 metal salt is selected from the group consisting of  
19 sodium, lithium, and potassium.
- 20 7. The composition of claim 1 wherein said ester comprises  
21 methyl acrylate.
- 22 8. The composition of claim 7 wherein the metal of said  
23 metal salt consists essentially of sodium.
- 24 9. The composition of claim 8 wherein said metal salt of  
25 acrylic or methacrylic acid comprises between about 1.9  
26 and about 7.5 mole percent of said copolymer.

- 1        10. The composition of claim 9 wherein said esters of  
2            alpha, beta-ethylenically-unsaturated carboxylic acid  
3            comprise between about 2.3 and about 7.4 mole percent  
4            of said copolymer.
- 5        11. The composition of claim 9 wherein said alkali metal  
6            salt of alpha, beta-ethylenically-unsaturated  
7            carboxylic acid comprises between about 3.0 and about  
8            6.5 mole percent of said copolymer.
- 9        12. The composition of claim 11 wherein said esters of  
10            alpha, beta-ethylenically-unsaturated carboxylic acid  
11            comprise between about 2.8 and about 6.3 mole percent  
12            of said copolymer.
- 13       13. The composition of claim 1 wherein the composition is  
14            acidified.
- 15       14. The composition of claim 13 wherein the acid is a  
16            polymeric acid.
- 17       15. The composition of claim 13 wherein the acid is  
18            phosphoric acid.
- 19       16. The composition of claim 1 wherein the composition has  
20            a 60° gloss of at least 100.
- 21       17. The composition of claim 1 wherein a strand, pellet, or  
22            film of the composition is acidified on its surface.
- 23       18. A composition produced by the process comprising:  
24            A) contacting:  
25                (1) a Group IA metal-containing solution with  
26                (2) a molten or fluid copolymer comprising alpha-  
27                olefins having from two to eight carbon atoms

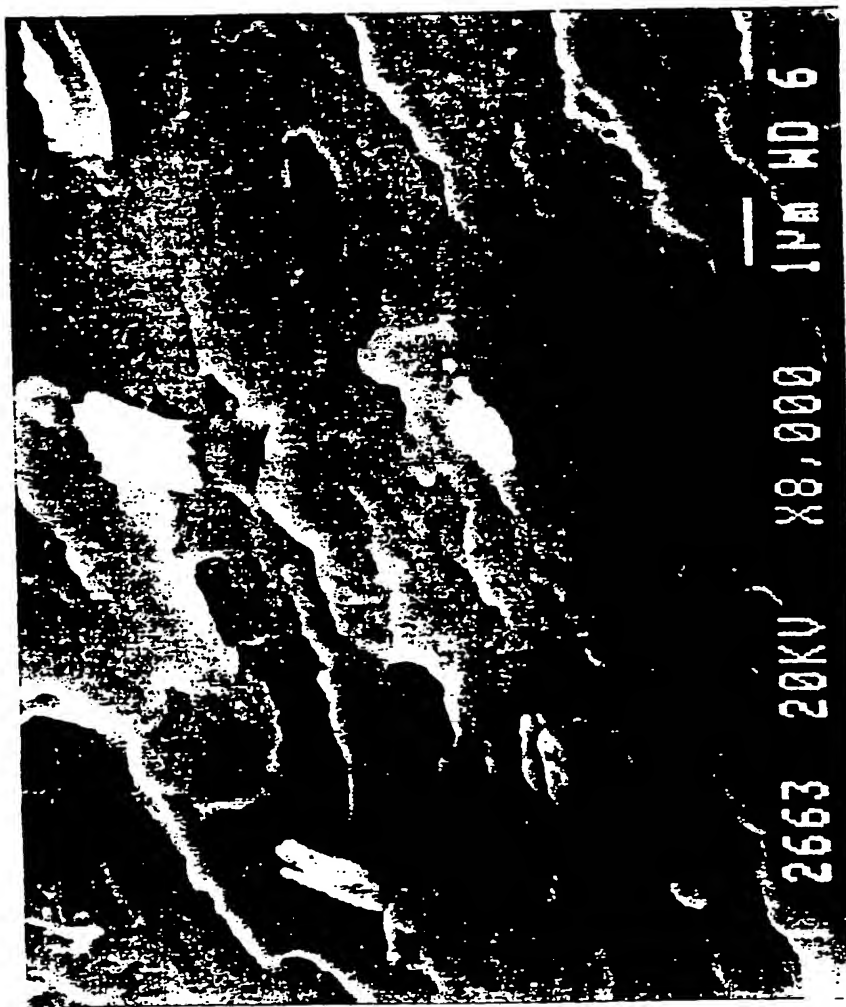
- 1 and esters of alpha, beta-ethylenically-  
2 unsaturated carboxylic acids having from four  
3 to twenty two carbon atoms and having a melt  
4 index between about 100 and about 2000 g/10  
5 min., as measured by ASTM method D 1239 at  
6 190°C; and  
7 B) intensively mixing the copolymer and Group IA  
8 metal-containing solution at a temperature and to  
9 an extent which provides an ionomer composition  
10 having no more than ten percent haze.
- 11 19. The composition of claim 18 wherein said copolymer  
12 comprises ethylene methyl acrylate copolymer.
- 13 20. The composition of claim 19 wherein said copolymer has  
14 a melt index between 300 and 600 g/10 min.
- 15 21. The composition of claim 18 wherein the Group IA metal-  
16 containing solution used to make the composition  
17 comprises aqueous metal hydroxide, where the metal is  
18 selected from the group consisting of sodium and  
19 potassium.
- 20 22. The composition of claim 21 wherein the concentration  
21 of metal hydroxide in the aqueous metal hydroxide used  
22 to make the composition is at least 50 percent by  
23 weight.
- 24 23. The composition of claim 18 wherein the intensive  
25 mixing in the process used to make the composition is  
26 provided by a twin-screw extruder.
- 27 24. The composition of claim 18 wherein the intensive  
28 mixing in the process used to make the composition  
29 occurs at a temperature between 200 and 350°C.

- 1        25. The composition of claim 24 wherein the temperature in  
2        the process used to make the composition is between  
3        about 275 and about 350°C.
- 4        26. The composition of claim 18 wherein the ionomer  
5        composition is substantially free of ionic clusters  
6        greater than 0.05 micron in size.
- 7        27. A film comprising the composition of claim 1.
- 8        28. The film of claim 27 wherein said film comprises at  
9        least two layers, a first layer selected from the group  
10       consisting of polypropylene, polyethylene,  
11       polyethylene, linear low density polyethylene, and  
12       nylon and a second layer comprising the composition of  
13       claim 1.
- 14       29. The film of claim 27 wherein said film has a thickness  
15       of no more than about 1 mil.
- 16       30. The film of claim 29 wherein said film has a thickness  
17       of no more than about 0.5 mil.
- 18       31. A blow-molded article comprising the composition of  
19       claim 1.
- 20       32. An easy-open package comprising the composition of  
21       claim 1.
- 22       33. A composition comprising a blend of the composition of  
23       claim 1 and a polymer selected from the group  
24       consisting of ethylene-alkyl acrylate copolymer,  
25       polypropylene, and high-density polyethylene.

- 1        34. A composition comprising the product of reacting (a)  
2        the composition of claim 1 and (b) a polymer selected  
3        from the group consisting of polyester, polyamide,  
4        polyurethane, and polycarbonate in the presence of  
5        sufficient acid to cross-link (a) and (b).
- 6        35. The composition of claim 34 wherein the reaction occurs  
7        in an extruder.
- 8        36. A composition comprising the product of  
9        transesterifying (a) the composition of claim 1 and (b)  
10       a polymer selected from the group consisting of  
11       ethylene alkyl acrylate copolymer, ethylene alkyl  
12       methacrylate copolymer, polyester, polyamide,  
13       polyurethane, and polycarbonate under  
14       transesterification conditions sufficient to cross-link  
15       (a) and (b).
- 16       37. The composition of claim 36 wherein the reaction occurs  
17       in an extruder.

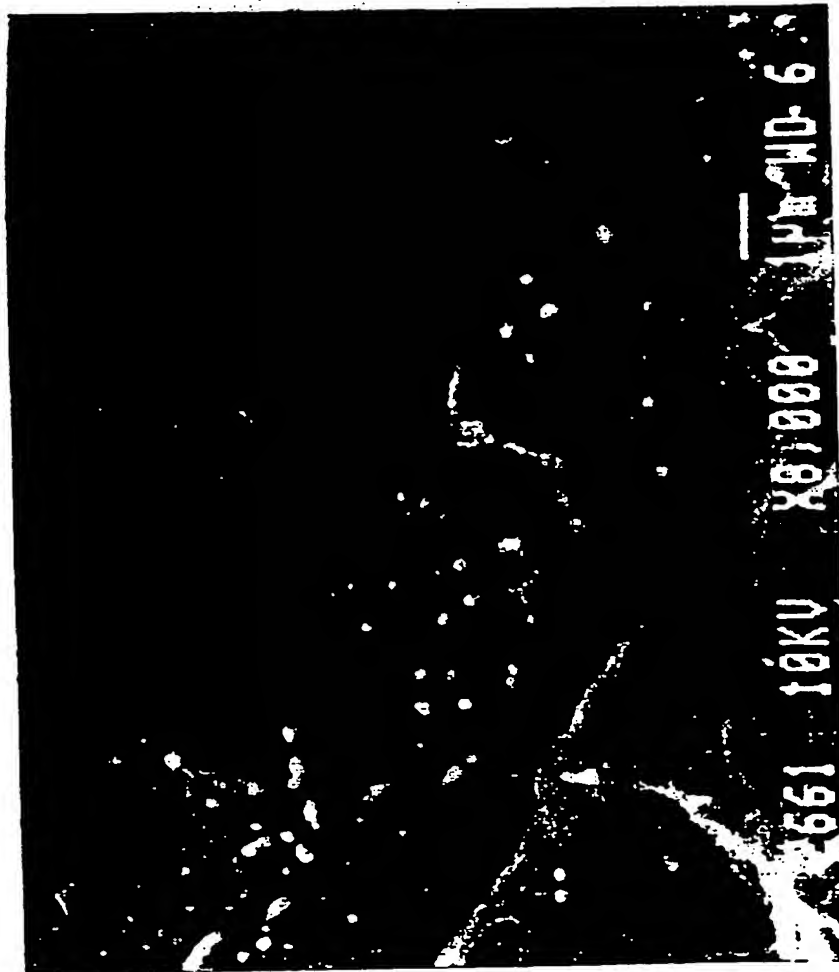
1/4

FIGURE 1



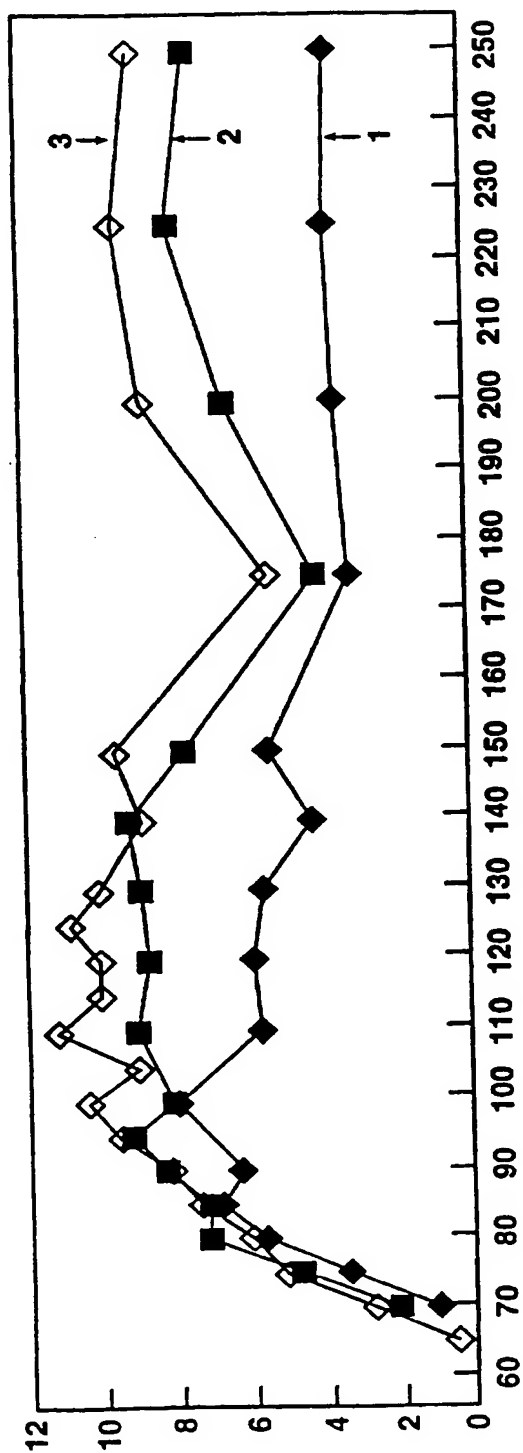
2/4

FIGURE 2



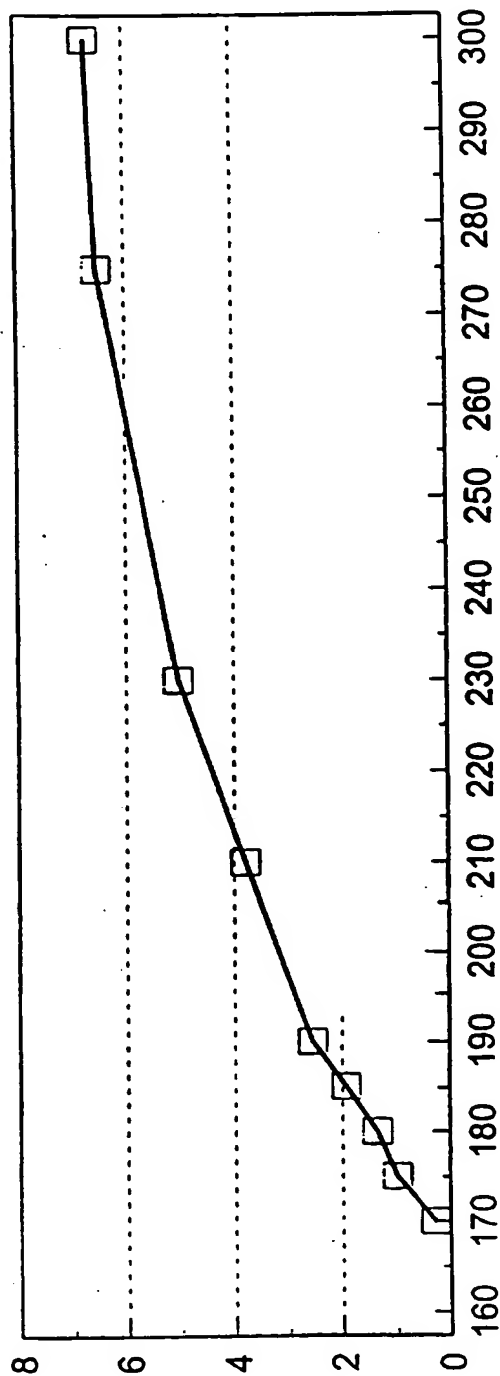
3/4

FIGURE 3



4/4

FIGURE 4



# INTERNATIONAL SEARCH REPORT

Interr. Application No  
PCT/US 96/01130

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08F210/02 C08F8/44 C08F8/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A,93 01219 (CHEVRON RESEARCH AND TECHNOLOGY COMPANY) 21 January 1993 cited in the application see page 7, line 23 - page 9, line 16 see page 9, line 24 - line 34 see page 10, line 1 - page 11, line 4; claims 1-15	1-37
Y	WO,A,93 06137 (CHEVRON RESEARCH AND TECHNOLOGY COMPANY) 1 April 1993 cited in the application see page 29, line 17 - page 33, line 18; claims 1-24,28-50	1-37
Y	DE,A,40 20 441 (HOECHST AG) 2 January 1992 see page 3, line 28 - line 34; claims 1-9	1-37
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

24 May 1996

Date of mailing of the international search report

12 06 96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Permentier, W

## INTERNATIONAL SEARCH REPORT

Intern. Application No  
PCT/US 96/01130

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 349 828 (BASF AG) 10 January 1990 cited in the application see page 2, line 33 - line 54; claims 1-8 ---	1
A	DATABASE WPI Section Ch, Week 9548 Derwent Publications Ltd., London, GB; Class A17, AN 93-088743 XP002003889 & JP,A,05 032 798 (SHINETSU POLYMER CO) , 9 February 1993 see abstract ---	1
A	DE,A,42 35 621 (BASF AG) 6 May 1993 see claims 1-4 ---	1
A	FR,A,2 304 624 (SUMITOMO CHEMICAL COMPANY, LTD.) 15 October 1976 cited in the application see page 5, line 7 - page 6, line 10; claims 1-6 ---	1,27,28
A	CHEMICAL ABSTRACTS, vol. 101, no. 18, October 1984 Columbus, Ohio, US; abstract no. 152575h, "ION-CROSSLINKED ETHYLENE COPOLYMERS" page 16; column 2; XP002003888 see abstract & JP,A,59 102 901 (NIPPON PETROCHEMICALS CO., LTD.) 14 June 1984 ---	1
P,X	WO,A,95 11929 (CHEVRON CHEMICAL COMPANY) 4 May 1995 see the whole document -----	1-37

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 96/01130

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9301219	21-01-93	US-A- 5218057 EP-A- 0548352 JP-T- 6501519	08-06-93 30-06-93 17-02-94
WO-A-9306137	01-04-93	AU-B- 3900293 CA-A- 2119575 EP-A- 0605643 FI-A- 941342 NO-A- 941051	28-07-93 01-04-93 13-07-94 23-03-94 23-03-94
DE-A-4020441	02-01-92	NONE	
EP-A-349828	10-01-90	DE-A- 3822069 JP-A- 2047111 US-A- 5003001	18-01-90 16-02-90 26-03-91
DE-A-4235621	06-05-93	NONE	
FR-A-2304624	15-10-76	JP-C- 951552 JP-A- 51107392 JP-B- 52023673 CA-A- 1064196 DE-A- 2611332 GB-A- 1504845 NL-A- 7602873 US-A- 4042766	25-05-79 22-09-76 25-06-77 09-10-79 07-10-76 22-03-78 21-09-76 16-08-77
WO-A-9511929	04-05-95	AU-B- 1084495	22-05-95

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:



**BLACK BORDERS**



**IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**



**FADED TEXT OR DRAWING**



**BLURRED OR ILLEGIBLE TEXT OR DRAWING**



**SKEWED/SLANTED IMAGES**



**COLOR OR BLACK AND WHITE PHOTOGRAPHS**



**GRAY SCALE DOCUMENTS**



**LINES OR MARKS ON ORIGINAL DOCUMENT**



**REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**



**OTHER: \_\_\_\_\_**

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**